Bulletin 630

Bureau of Mines

MINERAL FACTS AND PROBLEMS

1965 edition

By Staff, Bureau of Mines

UNITED STATES DEPARTMENT OF THE INTERIOR

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UNITED STATES DEPARTMENT OF THE INTERIOR
Stewart L. Udall, Secretary

BUREAU OF MINES
Frank C. Memmott, Acting Director

Created in 1849, the Department of the Interior—a Department of Conservation—is concerned with the management, conservation, and development of the Nation's water, fish, wildlife, mineral, forest, and park and recreational resources. It also has major responsibilities for Indian and Territorial affairs.

As the Nation's principal conservation agency, the Department works to assure that nonrenewable resources are developed and used wisely, that park and recreational resources are conserved for the future, and that renewable resources make their full contribution to the progress, prosperity, and security of the United States—now and in the future.

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Foreword

This edition of Mineral Facts and Problems marks the second revision of this widely used reference work. Events have shown that the 5-year interval between editions was well chosen. For many commodities there have been significant shifts in the past 5 years in the world supply-demand position and the production-consumption pattern, resulting both from political and social changes and from advances in science and technology. Despite such major shifts for some commodities, much of the background information presented in the 1960 edition of Mineral Facts and Problems remains pertinent. Hence, substantial portions of the carefully prepared and reviewed material from the previous edition remain unchanged in this edition.

The initial edition of Mineral Facts and Problems, published early in 1956, was an outgrowth of a Bureau of Mines commodity program statement series. The statements, revised periodically to reflect the rapidly changing positions of individual commodities in relation to national demands, provided broad basic and background information from which the Bureau could generate and evaluate ideas for mineral resource development and research investigations. This orderly presentation of mineral information proved useful to other Government organizations, commercial analysts, and educators and students. The Bureau hopes that this edition, Bulletin 630, also will prove as worthwhile a reference and as helpful in understanding and attacking the problems encountered in developing world mineral resources to meet mankind's material needs.

Like its predecessors, this edition represents the work of Bureau specialists—but it depends heavily on information from industry and reviews by critics in both industry and Government for which the Bureau is deeply appreciative. Technical editing of the volume was carried out by Paul Yopes and statistical editing by Kathleen J. D'Amico, both of the Division of Minerals.

PAUL ZINNER
Assistant Director, Mineral Resource Development

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INTRODUCTION

By Charles W. Merrill [1]

THE INDUSTRIAL strength and the security of the United States require an adequate, dependable, and continuing supply of raw materials, of which minerals constitute an indispensable segment. With an expanding population, a rising standard of living, and the instability inherent in a constantly changing international situation, the mineral supply outlook is a major national concern.

Structures, roads, and machines are built largely of mineral products; the energy to heat the structures and to power the machines is derived mostly from minerals; agricultural output is sustained with the aid of mineral fertilizers; and the Nation's economic and military security both are founded ultimately on its ability to obtain and utilize essential metals, nonmetals, and mineral fuels.

Mineral supply presents certain problems that are not common to raw materials derived from vegetable and animal sources. Minerals as mined are a one-time crop, whereas the products of agriculture, grazing land, forests, and fisheries continue to be available indefinitely under proper husbandry. Nevertheless, with minerals the possibilities of discovery and the potential inherent in an advancing technology frequently assure the replenishment of depleted reserves. For example, proved recoverable reserves of petroleum in the United States have remained for many years at about 12 times the annual rate of production, despite increasing output. This maintenance of the reserve level has resulted both from discovery of new oil pools and from improved techniques that make possible higher ultimate recovery from known deposits. Likewise, the ore reserves for many metals have been sustained by improved technology that has made it profitable to mine material of lower and lower grade.

Reclamation is an important factor in extending mineral supply. For example, although the gasoline powering an automobile and the lead added to it are consumed beyond reclamation, the lead that makes up much of the same automobile's battery has an extended life because about 85 percent of all lead in such batteries is reclaimed and used again.

To assure a future supply of minerals, the facts about minerals must be ascertained. The mineral problems of today must be identified, and those of tomorrow anticipated. Preparation must be made to attack any impediment to meeting the Nation's mineral requirements—by prospecting for new ore bodies, by research to find improved extractive, processing, and utilization methods, and by making abundant resources substitute effectively for those that are scarce. In short, all available knowledge, foresight, energy, and wisdom must be enlisted to assure the present generation, and those that are to follow, a mineral-resource base on which the United States can continue to build.

MINERAL PROBLEMS

The problems reported constitute obstacles to achievement of major objectives of industry and Government. These objectives are (1) wise production and utilization of U.S. mineral resources, (2) discovery and development of new sources of mineral supply, (3) maintenance of mineral reserves and stocks at adequate levels, (4) fostering a producing and processing industrial capacity large and flexible enough to exploit effectively the domestic mineral resources consonant with all foreseen requirements, and (5) assurance of access to foreign mineral supply to supplement domestic output as needed.

In facing the problems likely to be encountered in the pursuit of these broad objectives, five areas require development and analysis.

[1] Chief, Division of Minerals.

APPRAISAL OF MINERAL POSITION

Major decisions in industrial development and expansion, foreign affairs, international trade, defense, and many other areas frequently require reliable and comprehensive information on the Nation's mineral position. Government agencies charged with conducting U.S. foreign affairs, as well as those charged with procuring materials for defense and other domestic requirements, must know the country's mineral position. The Congress also depends on objective, authentic information so that its legislative decisions may be based on facts. Perhaps most important is an informed private industry, because it is the source of many major decisions involving minerals.

DEVELOPMENT OF SUBMARGINAL RESOURCES

Many deposits in the United States contain such a small percentage of the desired metal or mineral, or are so difficult to treat with present methods, that exploitation would not be profitable. Such deposits are classified as submarginal resources. If technologic history can be accepted as a guide, some of these deposits will be mined when the need becomes great enough or when new technologies make their extraction economically feasible. Some mineral commodities now supplied by importation occur domestically in submarginal deposits so large that the United States could become self-sufficient if cheaper production methods could be devised or if the price of the commodity rose.

The United States undoubtedly contains many submarginal deposits not yet discovered, or at least not delineated. There has been little commercial incentive to search for them or to develop those found in the course of other activities. Nevertheless, a demonstration of very large quantities of material, even if presumably of submarginal quality, is a powerful incentive to private enterprise to attempt commercial development. The early phases of research in submarginal resources often fall to Government, but privately financed organizations frequently undertake such development long before profitable operation can be assured. An example of this type of resource is the oil shale in Colorado and neighboring States, assaying 10 gallons or more per ton, that would yield an estimated 2 trillion barrels of oil if all of it now known could be processed.

POSSIBLE NEW OR WIDER USES FOR ABUNDANT RESOURCES

The United States has large deposits of mineral raw materials for which comparatively little use has been found but which may have applications that are yet to be discovered, for example, before World War II sea water, brines, magnesite, and dolomite, now used as sources of magnesium, were little used. Means that would expand the use of the metals or minerals in such deposits could relieve a serious drain on materials now in short supply that are required in some products and processes. Outstanding examples of plentiful but almost unused resources with promising possibilities are high-alumina clay and anorthosite, raw materials for production of aluminum, and vast reserves of lignite and peat as sources of energy. Furthermore, if commercial application for an abundant but little-used material were devised and demonstrated, a firm foundation would be laid for a new industrial enterprise. Titanium and helium are examples of resources that for many years were in the little-used category.

ALTERNATES

Development of substitutes is one way to improve the mineral position of the United States. Metals, minerals, and mineral fuels in ample supply can be substituted, under certain conditions, for those in scant supply. The maintenance of the German war machine during World War II on liquid fuels synthesized from coal is a spectacular example of substitution in time of stringency. In the United States the increasing substitution of aluminum for tin in tubes and foil has replaced an imported and relatively scarce metal with one in abundant domestic supply. The use, where practicable, of noncoking coals for steam generation in lieu of scarcer fuels that have important and singular use characteristics represents wise substitution. Each substitution of a plentiful mineral for a scarce one strengthens the Nation's position.

CONSERVATION

Basically, conservation entails wise use—not hoarding. Wise use in the mineral field in turn requires high eventual recovery of material from the ground and of the valuable constituents of such material; recovery at the time needed; fabrication or other preparation for use with minimum waste or loss of the valuable

material; efficient utilization through superior design in fabrication or high energy conversion in combustion; high recovery of coproducts and byproducts or storage of wastes for later treatment; application to purposes of high economic utility; and utilization of substitutes, where available, for other important materials that either are in limited reserve or have singular use characteristics not common to other minerals.

PROBLEM ATTACK—OBJECTIVE ACHIEVEMENT

Before attacking the problems of specific mineral commodities, relevant facts must be assembled and reviewed. The 88 chapters of this volume, each devoted to a mineral commodity or a group of closely related commodities, consist largely of a presentation of facts arranged in a standard pattern. The size, organization, and distribution of the industry are outlined; its technology briefed; byproducts, coproducts, substitutes, synthetics, and secondary products covered; reserves estimated; uses described; strategic and defense considerations reviewed; prices, costs, taxes and tariffs, and their trends presented; and other salient statistics and statistical trends set forth. Finally an outlook section is presented, and current and foreseen problems are identified.

The attacks on mineral problems may be simple and direct, or they make take the form of a broad, scientific assault on the unknown in the expectation that new knowledge will provide keys to the solution of problems both old and new. Thus the avenues of attack on mineral problems range from basic or pure research on the properties of minerals to the testing of specific ores as to their amenability to particular processes. Also of great importance is the distinction between technical feasibility without regard to economic feasibility and commercial or industrial applicability. Laboratory-scale work oriented to technical feasibility is usually classed as research. Beyond that stage comes engineering evaluation. Frequently there also must be investigations in pilot and demonstration plants before the ultimate design of commercial installations. These latter stages along with market analyses and consideration of other economic factors lie in the field of mineral-industry studies.

Research to acquire knowledge is the province of the scientist, whereas the job of applying knowledge to solve industrial problems lies largely with the engineer.

RESEARCH

Research in metallic or nonmetallic minerals, coal, petroleum, or natural gas may be undertaken separately, but all have problems in common and the scope and magnitude of effort in each field should be guided by their interrelationship. Industry, largely because its units are normally specialized as to both commodities and functions, will not or cannot use the comprehensive approach easily available to the Government. Thus Government has a unique role in coordinating and integrating research in the mineral industry.

In bringing mineral resources into man's service, aggressive research—from basic science through applied technology and including economic investigation—must characterize all stages, first in determining where and how best to explore and then on through exploration, development, production, processing, refining, utilization, marketing, and reclamation for reuse.

In nonfuel minerals, research is needed on exploration devices and techniques and on development drilling; physical research is needed on new materials. Equally urgent is the need for effective research in mining technology (mining methods, mechanization, transportation, rock breaking, loading, and integration of operation) and in milling, preparation, and beneficiating technology (crushing and grinding, flotation and gravity concentration, magnetic and electrostatic concentration, pneumatic methods, flowsheet development, and tailings disposal).

Metal extraction embraces smelting (furnace design, temperature control, atmospheric control, and slag and melt composition), hydrometallurgy and chemical processing (leaching, filtering, and electrolytic and chemical precipitation), nodulizing and briquetting, refining, and combinations of these and other techniques under special circumstances. Similar processing is involved in many minerals, particularly those of the nonmetal group. In all extractive metallurgy there is special need for research in making low-grade and refractory ore deposits available for use.

Recovery of scrap and its preparation for reuse are highly important phases of conservation of resources. Research can increase the efficiency of scrap processing.

In mineral-fuel research, more effective utilization of coal may be brought about by developing a larger and cheaper supply through more economical mining methods. Whereas generation of electricity and high-temperature

coking now provide the main markets for coal, perfection of processes under study—some of which have been or are now being used on an industrial scale—may create or expand demand for this abundant mineral as a source of organic chemicals, fertilizers, high calorific value gas, liquid fuels, and oils. Among the processes receiving great attention are direct hydrogenation, low-temperature carbonization, and gasification with subsequent utilization in the methanation reaction or the ammonia, the oxo, or the Fischer-Tropsch synthesis.

In petroleum and natural gas research, there are equal and parallel needs to meet. Improved drilling equipment and techniques will continue to offset costs of deeper drilling and rising ratios of drilling to discovery. Better methods of production (pressure maintenance, water flooding, in situ combustion, use of detergents, and utilization) will make available material now discounted in reserve estimates. Separation, identification, and characterization of the component parts of crude petroleum and natural gas will provide a sound basis for meeting changes in requirements for the end uses of these materials. Research also is the key to commercial utilization of the enormous U.S. oil shale resource.

MINERAL INDUSTRY STUDIES

The ever-changing mineral needs of industry and defense, supplied by sources subject to depletion by exploitation and to replenishment by discovery and development, require that the results of successful scientific and technologic research be applied aggressively and unremittingly to the mineral-supply situation. Wise and efficient use of natural resources depends to a large measure on resource factfinding as carried on in the field by geologists and exploration engineers and on advances in technology of mining and metallurgical extraction.

Increased mineral utilization is fostered by mineral-industry studies that point out commercial opportunities resulting from scientific and technical discoveries affecting minerals and from economic advances in other fields. Consumers and communities have new opportunities in many fields, provided by discovery of ore bodies, proof of sizable reserves, development of new or more efficient extraction methods, and new or improved sources of energy from mineral fuels to convert such ores to useful products.

On the other hand, increasing populations, advancing industrialization, new applications, and other elements of demand will call for a review of latent or partly developed resources as a new or expanded source of supply. New facilities like roads, railroads, canals, electric powerlines, natural gas pipelines, and other such developments may call for a reassessment of local mineral resources and the marketability of their products. Mineral-industry studies concentrate on such problems of supply and demand adjustment on a local, regional, or national basis as appropriate.

BASIC ECONOMIC TRENDS

The mineral industries have much in common with each other and with all other industry. The whole economy shares in such changes as growing demand based on population increase, rising gross national product, deflation and inflation of the currency, and several other shifting factors. The accompanying tables 1 to 6 and figures 1 to 6 present such data either directly or as indexes and in some instances include projections. The trends set forth have been basic to much of the commodity forecasting to be found in the "Outlook" sections of the commodity chapters.

TABLE 1.—*Population and total labor force of the United States* [1]

[Millions]

Year	Population	Labor force
1790	3.9	
1800	5.3	
1810	7.2	
1820	9.6	
1830	12.9	
1840	17.1	
1850	23.2	
1860	31.4	
1870	39.8	
1880	50.2	
1890	62.9	
1900	76.1	29.0
1901	77.6	30.0
1902	79.2	30.9
1903	80.6	31.8
1904	82.2	32.6
1905	83.8	33.7
1906	85.4	34.8
1907	87.0	35.6
1908	88.7	36.6
1909	90.5	37.5
1910	92.4	38.1
1911	93.9	38.7
1912	95.3	39.1
1913	97.2	39.5
1914	99.1	39.8
1915	100.5	40.1
1916	102.0	40.3
1917	103.3	42.7
1918	103.2	44.2
1919	104.5	42.0
1920	106.5	41.9
1921	108.5	42.4
1922	110.1	43.0
1923	112.0	43.8
1924	114.1	44.5
1925	115.8	45.0
1926	117.4	46.0
1927	119.0	46.9
1928	120.5	47.9
1929	121.8	49.4
1930	123.2	50.1
1931	124.1	50.7
1932	124.9	51.3
1933	125.7	51.8
1934	126.5	52.5
1935	127.4	53.1
1936	128.2	53.7
1937	129.0	54.3
1938	130.0	55.0
1939	131.0	55.6
1940	132.1	56.2
1941	133.4	57.5
1942	134.9	60.4
1943	136.7	64.6
1944	138.4	66.0
1945	139.9	65.3
1946	141.4	61.0
1947	144.1	61.8
1948	146.6	62.9
1949	149.2	63.7
1950	151.7	64.7
1951	154.4	66.0
1952	157.0	66.6
1953	159.6	67.4
1954	162.4	67.8
1955	165.3	68.9
1956	168.2	70.4
1957	171.3	70.7
1958	174.2	71.3
1959	177.1	71.9
1960	180.7	73.1
1961	183.7	74.2
1962	186.6	74.7
1963	189.3	75.7
PROJECTIONS		
1965	195.4	78.1
1970	211.5	84.6
1975	229.0	91.6
1980	247.9	99.1

[1] This table incorporates some revisions from previous Mineral Facts and Problems (BuMines Bulletin 585).

Source: *Population.*—Department of Commerce, Bureau of the Census. Current Population Reports, Series P-25. Includes Armed Forces overseas beginning 1930 and Alaska and Hawaii beginning 1960. *Labor force 1900–28.*—National Industrial Conference Board. Economic Almanac. *Labor force, 1929–63.*—Department of Labor, Bureau of Labor Statistics. Employment and Earnings. Includes civilians employed, civilians unemployed and looking for work, and Armed Forces. Data for 1947–56 adjusted to reflect new definitions adopted in 1957. Beginning 1953, material from 1950 census introduced. Alaska and Hawaii included beginning 1960. Data from 1960 census introduced beginning 1962.

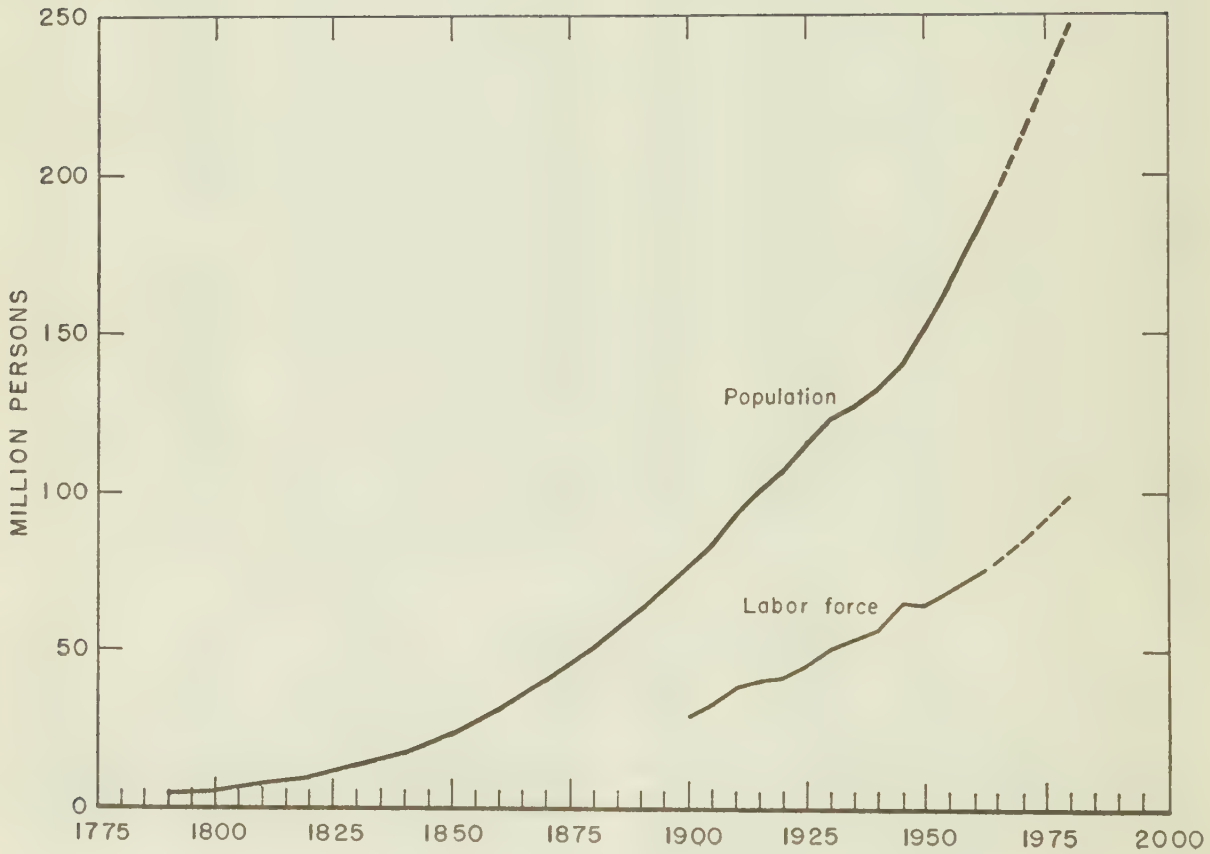

FIGURE 1.—Population and Total Labor Force of the United States.

TABLE 2.—*Gross national product*

[Billion 1954 dollars]

Year	Gross national product
1909	104.1
1910	106.8
1911	109.5
1912	116.1
1913	117.0
1914	112.1
1915	111.4
1916	120.0
1917	120.5
1918	132.9
1919	132.6
1920	125.6
1921	114.9
1922	133.2
1923	149.2
1924	149.0
1925	161.8
1926	170.8
1927	170.5
1928	171.8
1929	181.8
1930	164.5
1931	153.0
1932	130.1
1933	126.6
1934	138.5
1935	152.9
1936	173.3
1937	183.5
1938	175.1
1939	189.3
1940	205.8
1941	238.1
1942	266.9
1943	296.7
1944	317.9
1945	314.0
1946	282.5
1947	282.3
1948	293.1
1949	292.7
1950	318.1
1951	341.8
1952	353.5
1953	369.0
1954	363.1
1955	392.7
1956	400.9
1957	408.6
1958	401.3
1959	428.6
1960	439.9
1961	447.9
1962	476.4
1963	492.6
PROJECTIONS	
1965	531.0
1970	640.0
1975	771.0
1980	929.0

Source: Department of Commerce, Office of Business Economics. *1909–55.*—U.S. Income and Output, a supplement to the Survey of Current Business. 1958, pp. 118–119, 138–139. *1956–63.*—Survey of Current Business.

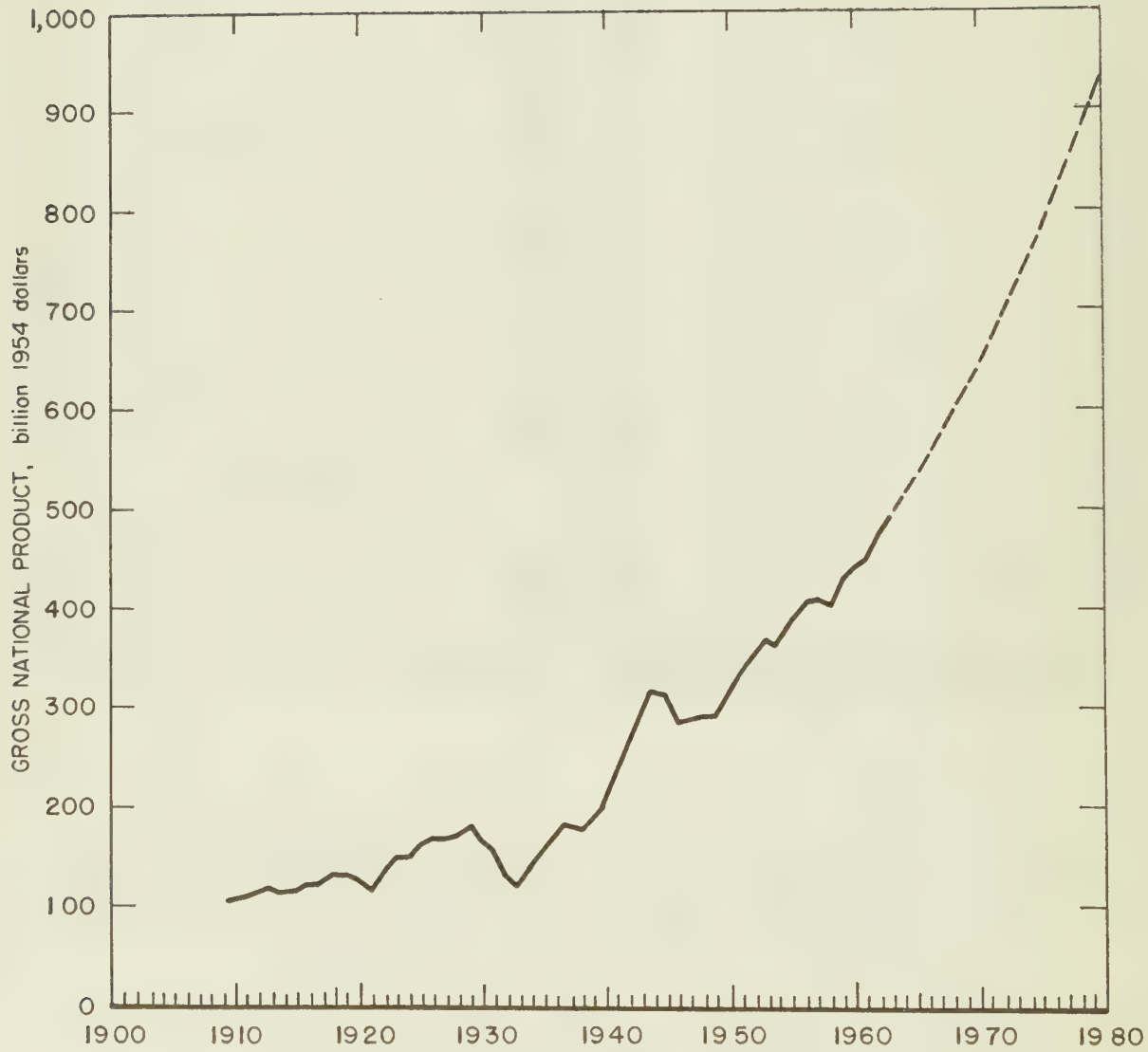

FIGURE 2.—Gross National Product for the United States.

TABLE 3.—*Construction activity in the United States*

[Billion 1954 dollars]

Year	New public	New private	Total construction [1]
1915	1.9	6.9	13.7
1916	1.7	7.6	14.0
1917	2.6	6.5	12.8
1918	3.8	5.0	12.8
1919	3.1	6.7	13.9
1920	1.9	7.4	13.3
1921	2.6	7.2	14.5
1922	3.0	10.7	18.8
1923	2.8	13.3	21.6
1924	3.3	14.7	23.9
1925	3.6	15.9	25.7
1926	3.6	17.2	27.4
1927	4.2	17.0	28.3
1928	4.3	16.0	27.1
1929	6.0	19.9	36.0
1930	7.3	14.8	31.5
1931	7.4	10.4	26.6
1932	6.1	5.5	19.6
1933	5.1	3.8	12.2
1934	6.6	4.5	20.1
1935	6.5	5.9	21.7
1936	10.1	8.6	29.6
1937	7.9	10.0	27.9
1938	8.7	9.2	27.9
1939	9.7	11.3	31.3
1940	9.0	12.7	31.9
1941	13.4	14.3	37.8
1942	22.5	7.1	39.3
1943	11.9	3.8	25.1
1944	5.5	3.9	18.8
1945	4.2	5.9	20.6
1946	3.3	16.3	32.9
1947	4.2	19.1	36.9
1948	5.4	21.5	41.2
1949	7.4	21.2	42.3
1950	8.0	26.2	48.1
1951	9.9	24.6	48.9
1952	11.0	24.3	49.6
1953	11.1	25.8	51.2
1954	11.7	27.6	54.3
1955	11.4	31.4	59.0
1956	11.7	30.1	58.0
1957	12.5	29.8	58.2
1958	13.6	29.3	58.7
1959	13.9	32.5	65.1
NEW SERIES			
1959	13.9	33.6	65.1
1960	13.6	32.2	63.5
1961	14.6	32.0	62.7
1962	14.3	34.3	65.3
1963	15.2	35.5	67.9
PROJECTIONS			
1965	16.9	38.8	74.1
1970	21.8	48.6	92.4
1975	28.2	60.9	115.1
1980	36.6	76.3	143.5

[1] Includes private and public new construction plus maintenance and repair. Data for maintenance and repair not available for 1961–63; Totals for these years were estimated.

Source: Department of Commerce and Department of Labor. New series beginning 1959 not strictly comparable with earlier data. Deflated to 1954 dollars by Division of Economic Analysis, Bureau of Mines

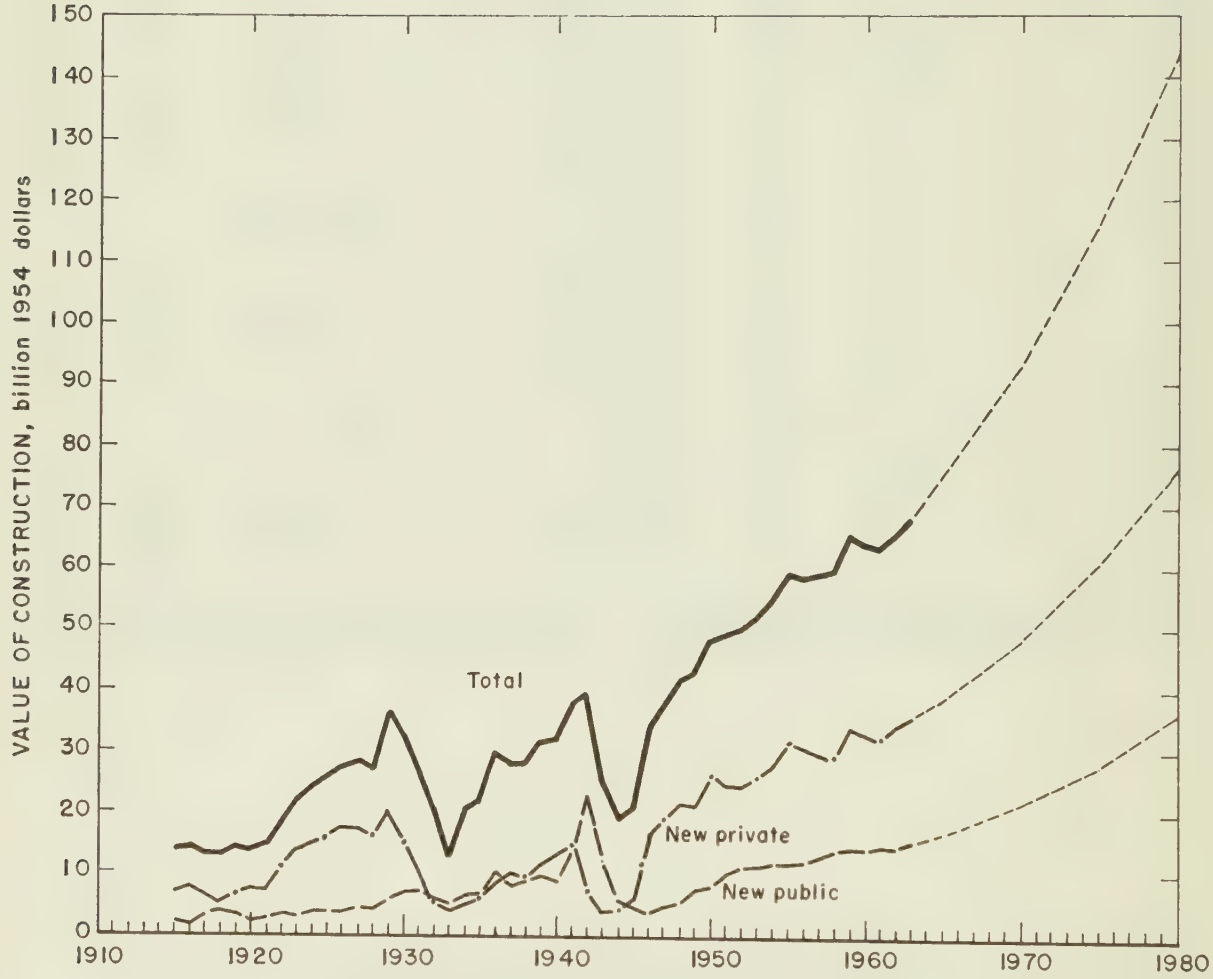

FIGURE 3.—Construction Activity in the United States.

TABLE 4.—*Federal Reserve Board index of industrial production*

[1957–59=100]

Year	Industrial production	Year	Industrial production
1919	24. 9	1946	59. 5
1920	26. 2	1947	65. 7
1921	20. 1	1948	68. 4
1922	25. 6	1949	64. 7
1923	30. 5	1950	74. 9
1924	28. 6	1951	81. 3
1925	31. 5	1952	84. 3
1926	33. 4	1953	91. 3
1927	33. 3	1954	85. 8
1928	34. 6	1955	96. 6
1929	38. 4	1956	99. 9
1930	32. 0	1957	100. 7
1931	26. 5	1958	93. 7
1932	20. 7	1959	105. 6
1933	24. 4	1960	108. 7
1934	26. 6	1961	109. 8
1935	30. 7	1962	118. 3
1936	36. 3	1963	124. 3
1937	39. 7		
1938	31. 4	PROJECTIONS	
1939	38. 3		
1940	43. 9		
1941	56. 4		
1942	69. 3	1965	135. 0
1943	82. 9	1970	165. 8
1944	81. 7	1975	203. 6
1945	70. 5	1980	250. 2

Source: *1919–61.*—Board of Governors of the Federal Reserve System. Industrial Production, 1957–59 Base, P. 8–149. *1962–63.*—Federal Reserve Bulletin 1964.

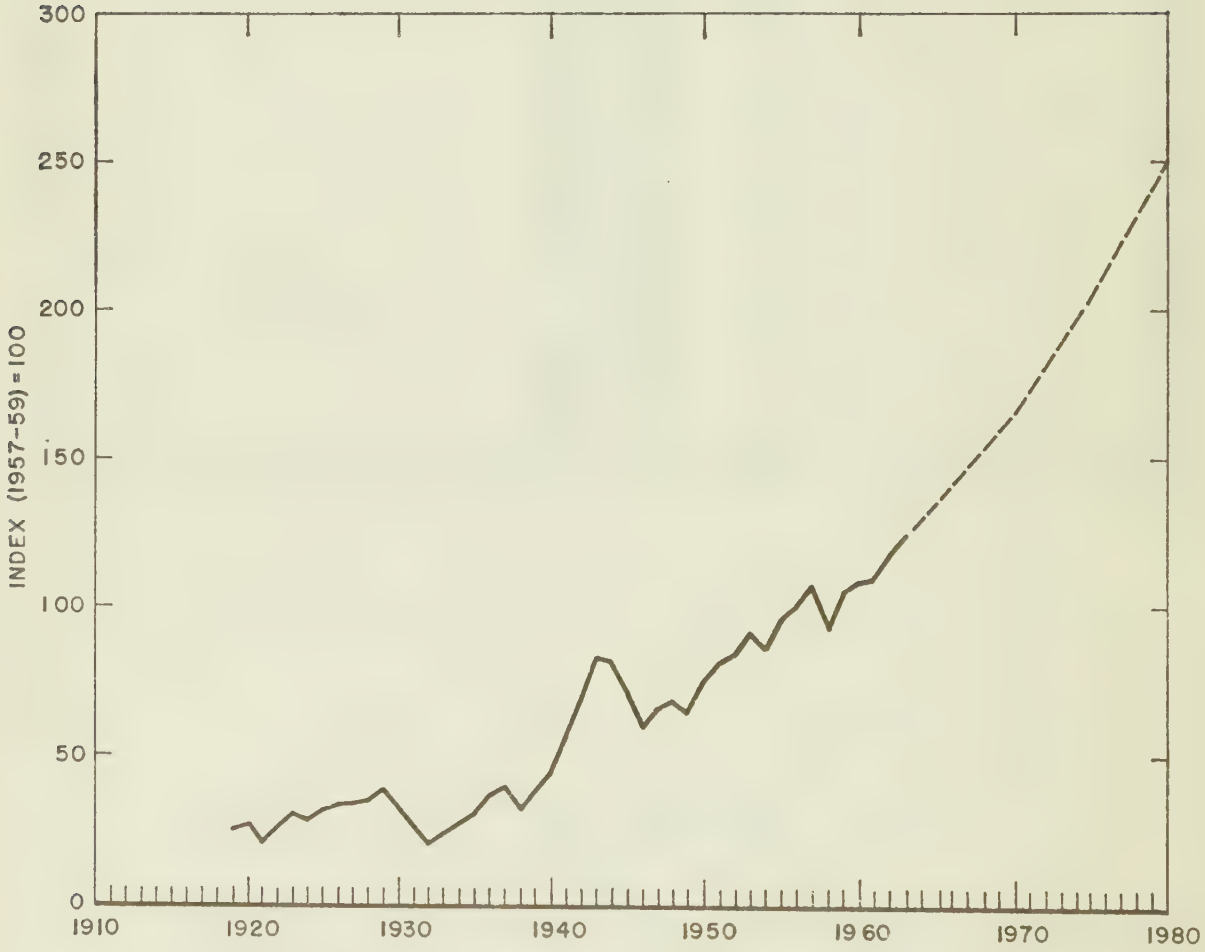

FIGURE 4.—Federal Reserve Board Index of Industrial Production.

TABLE 5.—*Consumers' and wholesale price indexes*

[1957–59=100]

Year	Consumers'	Wholesale	Year	Consumers'	Wholesale
1913	34.5	38.2	1939	48.4	42.2
1914	35.0	37.3	1940	48.8	43.0
1915	35.4	38.0	1941	51.3	47.8
1916	38.0	46.8	1942	56.8	54.0
1917	44.7	64.3	1943	60.3	56.5
1918	52.4	71.7	1944	61.3	56.9
1919	60.3	75.8	1945	62.7	57.9
1920	69.8	84.5	1946	68.0	66.1
1921	62.3	53.4	1947	77.8	81.2
1922	58.4	52.9	1948	83.8	87.9
1923	59.4	55.1	1949	83.0	83.5
1924	59.6	53.6	1950	83.8	86.8
1925	61.1	56.6	1951	90.5	96.7
1926	61.6	54.8	1952	92.5	94.0
1927	60.5	52.3	1953	93.2	92.7
1928	59.7	53.0	1954	93.6	92.9
1929	59.7	52.1	1955	93.3	93.2
1930	58.2	47.3	1956	94.7	96.2
1931	53.0	39.9	1957	98.0	99.0
1932	47.6	35.6	1958	100.7	100.4
1933	45.1	36.1	1959	101.5	100.6
1934	46.6	41.0	1960	103.1	100.7
1935	47.8	43.8	1961	104.2	100.3
1936	48.3	44.2	1962	105.4	100.6
1937	50.0	47.2	1963	106.7	100.3
1938	49.1	43.0			

Source: Department of Labor, Bureau of Labor Statistics. Series available in a number of sources including Economic Almanac, Statistical Abstract, Survey of Current Business, and Monthly Labor Review.

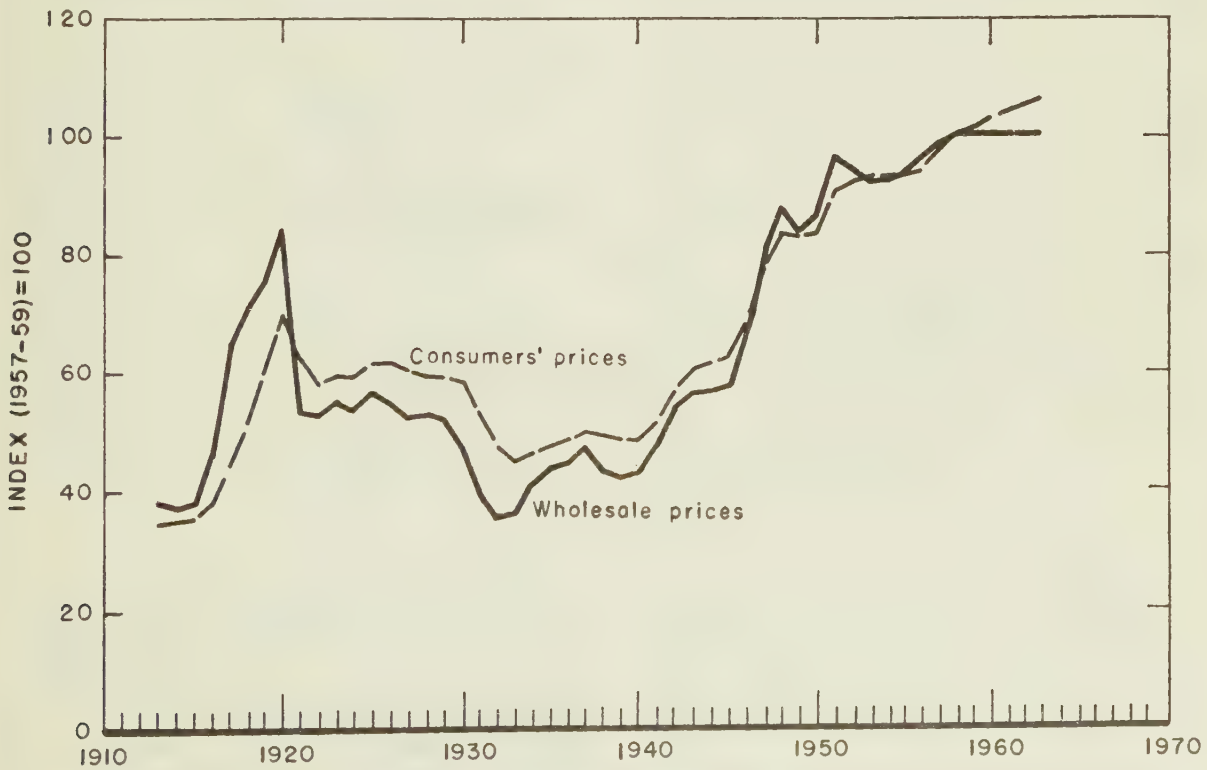

FIGURE 5.—Consumers' and Wholesale Price Indexes.

TABLE 6.—*Consumption of mineral-energy fuels and energy from waterpower*

Year	Total, trillion Btu	Per capita,[1] million Btu
1910	14, 800	160
1920	19, 782	186
1930	22, 288	181
1940	23, 908	181
1945	31, 541	225
1950	34, 153	225
1951	36, 913	239
1952	36, 576	233
1953	37, 697	236
1954	36, 360	224
1955	39, 956	242
1956	42, 007	250
1957	41, 920	245
1958	41, 493	238
1959	43, 411	246
1960	44, 960	249
1961	45, 724	249
1962	47, 897	257
1963	49, 816	263
PROJECTIONS		
1965	53, 326	273
1970	63, 110	298
1975	74, 010	323
1980	85, 934	347

[1] Based on population data in table 1.

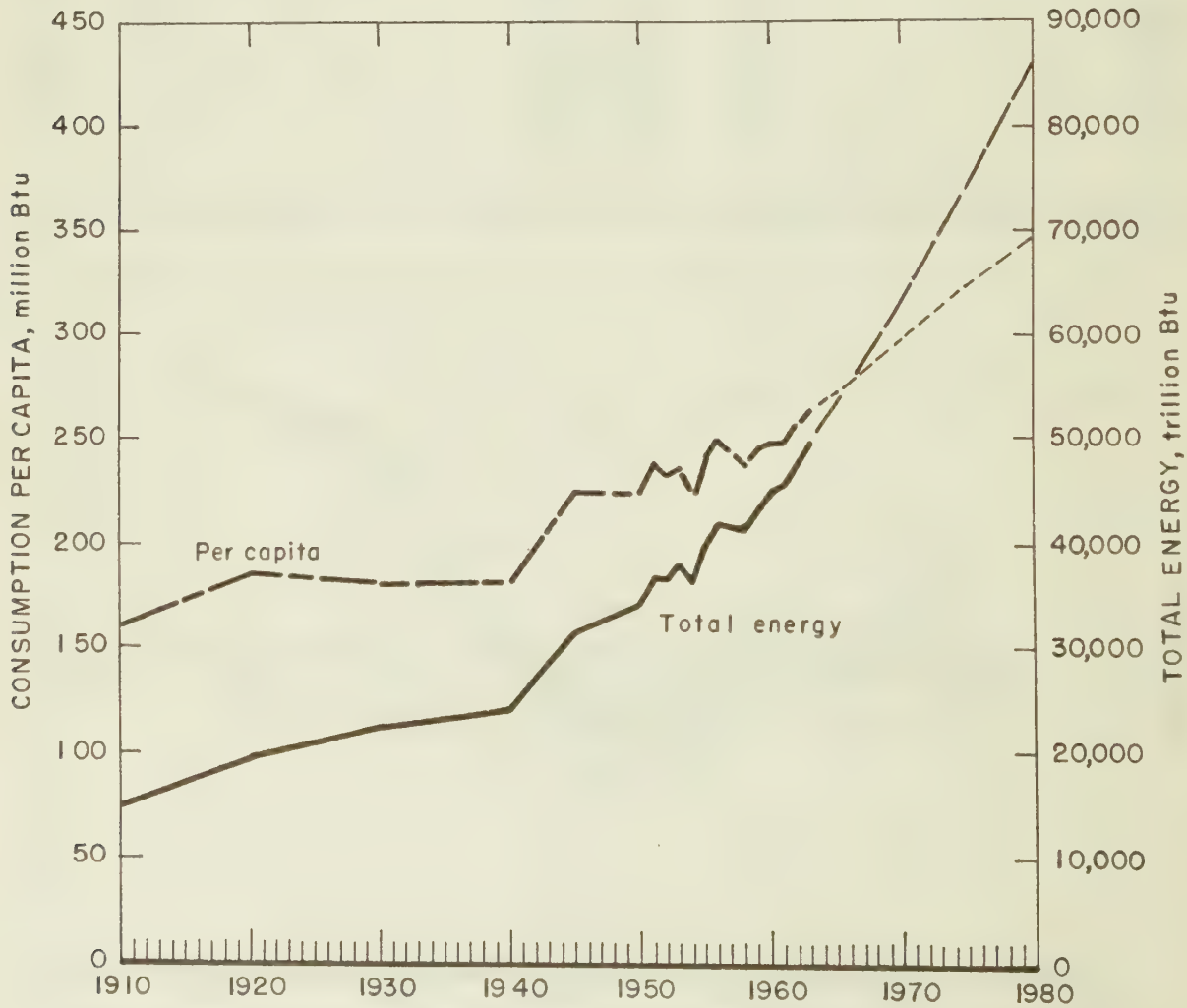

FIGURE 6.—Consumption of Mineral-Energy Fuels and Energy from Waterpower Related to Population.

ALUMINA AND BAUXITE

By Lloyd R. Williams [1]

ALUMINA (Al_2O_3), the raw material used for the production of aluminum, occurs widely and comprises about 15 percent of the earth's surface. However, only material identified as bauxite, in which the alumina has been concentrated by weathering processes, qualifies commercially as a source of alumina under present economic and technical conditions.

World consumption of alumina in 1963 was estimated at 13 million short tons; about 50 percent was consumed in North America and 41 percent in Europe. The consumption of alumina in the United States in 1963 was about 5 million tons and by 1980 annual consumption may be 18 million tons.

World bauxite production in 1963 was estimated at 29.8 million tons of which 51 percent was produced in the Western Hemisphere. About 94 percent of the bauxite consumed in the United States is used in alumina production and the remainder in making abrasive, chemical, and refractory products. Bauxite consumption in the United States was 11.3 million long dry tons in 1963 and by 1980 consumption may be 40 million tons.

Although the United States produces essentially all of its alumina requirements and is the world's largest consumer of bauxite, less than 15 percent of its bauxite requirement is produced domestically.

The domestic bauxite reserve which is mainly in Arkansas is estimated at 50 million tons averaging about 52 percent Al_2O_3. The reserve is too small to permit production to be expanded significantly. The total world reserve of bauxite at the end of 1963 was estimated at 5.8 billion tons with the largest deposits in Australia, Guinea, Jamaica, Hungary, Yugoslavia, Surinam, and Ghana.

As a result of improvements in technology it has been possible to reduce the grade of ore used in alumina plants. In 1930 ore used in the United States averaged 60 percent alumina, but by 1963 the average was less than 50 percent.

The average grade of ore treated probably will continue to decrease gradually, and successful application of processes now being tested could result in use of material containing less than 35 percent alumina.

Bauxite, an ore containing hydrated aluminum oxide minerals such as gibbsite, boehmite, or diaspore, is formed by weathering processes acting on alumina-bearing rocks. The largest deposits occur in tropical or subtropical climates and are at or near the surface. Most bauxite is mined by open-pit methods, but bauxite also is recovered by underground mining methods in the United States and in Europe.

Assurance of an adequate and dependable long-range supply of alumina requires discovery of new sources and the solution of numerous mining and metallurgical problems. A challenging problem is the development of a commercial process for producing alumina from domestic low-grade materials. Problems of the Bayer process include the need to improve its efficiency and development of methods for utilizing tailings. There is insufficient information on quantity, grade, and type of potential alumina resources, and exploration is handicapped by lack of a rapid method of analyzing for alumina. Mechanical beneficiation of low-grade bauxites is hampered by the high loss of alumina in removing iron and silica.

BACKGROUND

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

World bauxite production in 1963 was estimated at 29.8 million tons of which 51 percent was produced in the Western Hemisphere. Jamaica, Surinam, and British Guiana continue as the major producers in the Western Hemisphere. Although bauxite mining started as late as 1952 in Jamaica, the country became the major world producer in 1957 and continues to

[1] Commodity specialist.

maintain that position. Nearly half of the bauxite consumed in the United States in 1963 was produced in Jamaica.

World alumina consumption in 1963 was estimated at about 13 million tons, of which 38 percent was consumed in the United States, 41 percent in Europe, 12 percent in Canada, and 4 percent in Japan. In 1963 most of the alumina plants were in or near the consuming country. However, in recent years the tendency to build alumina plants near the source of the raw material to reduce transportation costs, has been evident. Aluminum producing companies operate most of the bauxite mines and own the alumina production facilities.

The actual and planned capacity and location of the U.S. alumina plants, their sources of bauxite, and the aluminum plants, that consume most of the alumina production are shown in figure 1.

Approximately 94 percent of the alumina shipments in 1963 went to the aluminum industry; the remainder was shipped to abrasive, refractory, chemical, or other plants.

Eight alumina plants used about 94 percent of the bauxite consumed in 1963. The remaining 6 percent was consumed by about 80 companies in about 200 plants including helium-producing plants and municipal waterworks. Three of the four alumina producers are vertically integrated from mining through production of semifabricated aluminium. Two of the integrated producers, Aluminum Company of America and Reynolds Metals Co. use both domestic and foreign bauxite. The third, Kaiser Aluminum & Chemical Corp., uses only foreign bauxite from its own mines. The fourth producer, Ormet Corp., uses bauxite purchased from a foreign source. In 1963 six independent companies produced bauxite in the United States on a small scale mainly for specialty uses. In Arkansas Campbell Bauxite Co. and Stauffer Chemical Co. produced dried bauxite. Activated bauxite was produced by these same two companies and Porocel Corp. Calcined bauxite was produced by American Cyanamid Co. In Alabama crude ore was shipped by Wilson-Snead Mining Co. (formerly D. M. Wilson Bauxite Co.). Dried bauxite was produced by R. E. Wilson Mining Co. and calcined bauxite was produced by Harbison-Walker Refractories Co. In Georgia, American Cyanamid Co. shipped crude ore and also produced dried bauxite. About 1 million tons of bauxite per year is consumed directly without passing through an intermediate alumina production stage. All of the ore from Alabama and Georgia is consumed directly together with some from Arkansas and a minor part of the imports.

Bauxite exports represented about 2 percent of the new supply of which 85 percent was imported.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Bauxite is a rock composed principally of the aluminum oxide minerals, gibbsite, boehmite, and diaspore. *Gibbsite* is a trihydrate ($Al_2O_3 \cdot 3H_2O$). *Boehmite* and *diaspore* are monohydrates ($Al_2O_3 \cdot H_2O$). Major impurities in the bauxite ores are iron oxides, aluminum silicates, and titanium oxides. Types of bauxite ores are generally identified as Jamaican, Surinam, and European. The *Jamaican type* is a mixture of both trihydrate and monohydrate minerals and containing about 50 percent Al_2O_3, 1 to 2 percent silica, and 20 to 30 percent iron oxide. The *Surinam type* is mainly the trihydrate gibbsite usually containing 50 percent or more Al_2O_3, 2 to 15 percent silica, and 5 to 15 percent iron oxide. The *European type* contains the monohydrates, boehmite and diaspore, and is about 55 percent alumina, 4 percent silica, and 10 to 20 percent iron oxide.

Crude bauxite is bauxite as mined containing from 5 to 25 percent free moisture.

Activated bauxite is used as an absorbant to refine sugar syrups and liquors, dehydrate and filter petroleum products, and act as a drying agent in industrial processes. It is processed by crushing and heating selected bauxite at 250° to 350° F to remove free water. After further crushing and screening it is thermally activated, the temperatures differ depending on the various uses of the product. The activated bauxite is cooled to 300° F and screened and deironed. It can be regenerated repeatedly for a number of cycles by controlled heating.

Dried bauxite is prepared by heating crude bauxite in a drying kiln at about 1,100° F for 15 to 40 minutes to reduce the free moisture to less than 1 percent. Uncontrolled heating may cause calcining and reduce the solubility of the alumina hydrate in the Bayer process.

Calcined bauxite for the abrasive and refractory industries is processed by heating in kilns at 1,700° to 2,900° F depending on use for about 1 to 1.5 hours to reduce total volatile matter including the chemically combined water in the ore to less than 1 percent. About 2 tons of crude ore produces 1 ton of calcined bauxite.

Bauxite specifications vary with plant and ultimate use. National stockpile specifications for all grades except chemical have been established (*3*).[2]

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

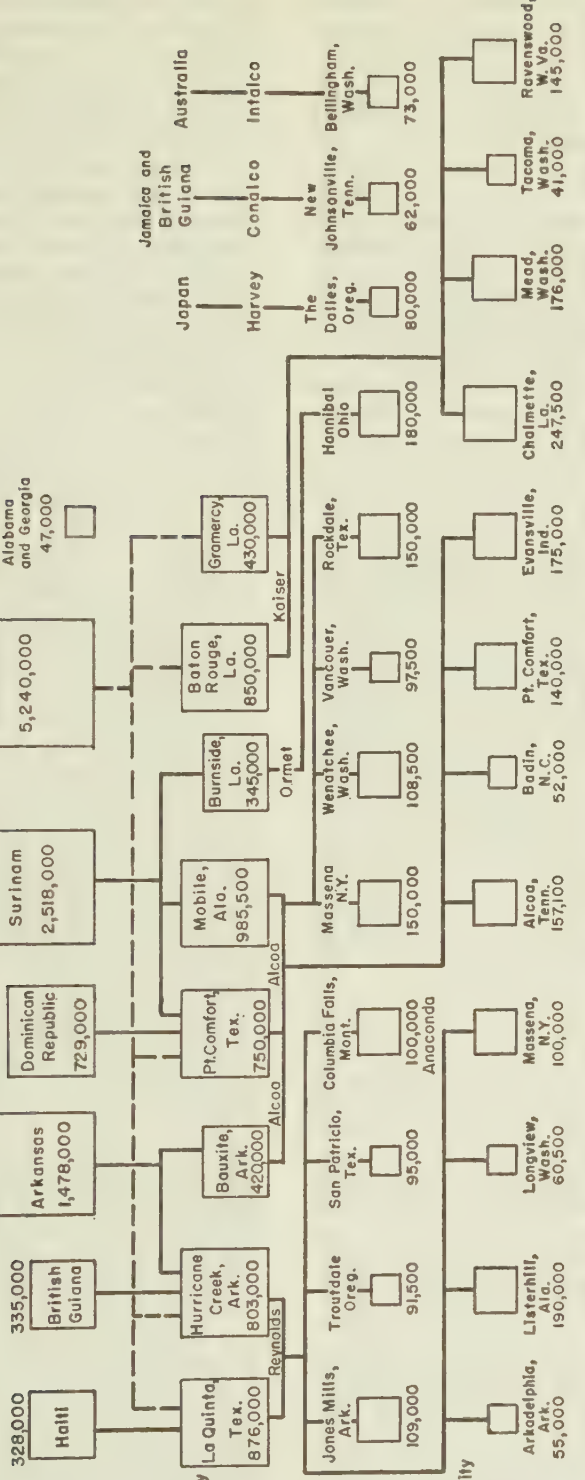

FIGURE 1.—Bauxite Supply and Alumina- and Aluminum-Plant Capacities in the United States in 1963 (Includes Plants Under Construction).

Table 1 gives the chemical analyses of bauxite used by the metallurgical, abrasive, chemical, and refractory industries.

TABLE 1.—*Chemical analysis of typical bauxites, by grade* [1]

[Percent]

Grade	Al_2O_3	SiO_2	Fe_2O_3	TiO_2
Metallurgical	50–55	0–15	5–30	
Abrasive	Min. 55	Max. 5	Max. 6	Min. 2.5
Chemical	Min. 55–58	Max. 5–12 [2]	Max. 2	
Refractory	Min. 59–61	Max. 1.5–5.5	Max. 2	Max. 2.5

[1] Most of the remainder represents water of crystallization.
[2] A major portion of the bauxite used by the U.S. chemical industry exceeds 15 percent.

Red mud the residue that results after alumina is extracted from bauxite by the Bayer process, consists largely of a complex sodium aluminum silicate and iron oxides. In the combination process the red mud is the feed to a subsequent lime-soda sinter step. The residue from the combination process is called *brown mud* or *sinter mud* and contains calcium silicates and iron oxides but little sodium aluminum silicate.

Alumina is aluminum oxide Al_2O_3, the calcined product of Bayer or combination processes. Corundum, emery, ruby, and sapphire are natural mineral forms. In the commercial form it is a fine white powder containing about 0.5 percent impurities. A typical analysis of alumina used in the production of aluminum follows:

	Percent
Chemical composition:	
Silica (SiO_2)	0.02
Iron oxide (Fe_2O_3)	.02
Titanium dioxide (TiO_2)	.003
Phosphorus pentoxide (P_2O_5)	Nil
Potash (K_2O)	Nil
Sulfur trioxide (SO_3)	Nil
Soda (Na_2O)	.45
Calcium oxide (CaO)	.02
Lead (Pb)	Nil
Alumina (Al_2O_3)	Bal.
Ignition loss and water absorption:	
Loss on ignition (1,000° C)	2.67
Water absorption (bone dry-basis)	3.16
Screen analysis (Tyler mesh):	
+48	Nil
−48+100	.5
−100+200	53.5
−200	46.0
−325 (wet on original sample)	12.0

Activated alumina is a highly porous and granular form of aluminum oxide having preferential adsorptive capacity for moisture from gases, vapors, and some liquids. When saturated it can be reactivated by the controlled application of heat within the range of 350° to 600° F to drive off the moisture. It is used as a drying agent, catalyst, or catalyst carrier.

Calcined alumina is a high-purity alpha-alumina produced by heating at 2,000° to 2,300° F hydrated alumina ($Al_2O_3 \cdot 3H_2O$) precipitated from soduim aluminate liquor in refining of bauxite ores by the Bayer process. Production of aluminum is the principal use of calcined alumina. Various grades of calcined alumina are produced under carefully controlled conditions for the manufacture of fused alumina abrasives and high-temperature refractories. High-grade ceramic shapes are made from alumina calcined at 2,700° to 2,900° F with a high melting point of 3,700° F and a hardness of 9 on Mohs' scale.

Tabular alumina, also Al_2O_3 is prepared by heating $Al_2O_3 \cdot 3H_2O$ to slightly below the fusion point of alumina (3,700° F). It is used in refractories, in insulators, and as a filter in plastics.

TECHNOLOGY

Geology and Exploration

Bauxite is formed by the weathering of alumina-bearing materials such as feldspars or clays. Ideal conditions, most likely to occur in wet tropical or subtropical climates, are nearly continual rainfall, constant warm temperatures, and relatively good drainage over a long period of time (*1*). The degree of acidity or alkalinity of the weathering solutions determines whether hydrated aluminum oxides or hydrated aluminum silicates form.

The Arkansas bauxite deposits were formed by weathering of nepheline syenite intrusions of Tertiary age during the period between the formation of the Midway marine clays and the deposition of the Saline formation of the Wilcox group of continental sediments. Some later transported deposits were formed in the unconsolidated clays and sands near the syenite stocks. The bauxite deposits in the Southeastern States were found within flat-lying kaolin bodies overlain by sand and clays of early Tertiary age.

In Jamaica large lateritic deposits were formed on karsted Tertiary limestones by reaction of oxygenated water and carbonic acid with sodium and calcium aluminum silicates to produce gibbsitic bauxite. The deposits are soft, uniformly porous and dark-red or yellow to white and are found in solution pockets, sinkholes, and troughs on the uneven eroded surface of Oligocene and lower Miocene calcareous limestones (*12*).

In Europe the formation of bauxite extended from Triassic through Cretaceous and Tertiary time. The boehmitic and diasporic deposits in France and Greece are residuals on top of lower Cretaceous limestones. Bauxite deposits in British Guiana and Surinam lie on top of Precambrian clays and are covered by tertiary sands and clays. They were formed by leaching actions on kaolin in material transported to low-

land areas from upland weathered metamorphic and igneous rocks.

Western African bauxite deposits usually are associated with the weathering of schistose rocks, and Indian and Australian bauxites are associated with basalts.

Many of the bauxite deposits are covered by little, if any, overburden. Prospecting is done along the unconformable surfaces on which the weathering interval was suitable for the formation of bauxite. There is no rapid method of chemical analysis for alumina, but differential thermal methods have been developed for quick approximations of the kaolinite and gibbsite content of samples.

Since bauxite forms by weathering, deposits usually are nearly horizontal and lie close to the surface. Initial drilling is done at 400- to 4,000-foot intervals, depending on the depth and continuity of the deposit.

Mining

Open-pit mining accounts for 88 percent of the bauxite produced in the United States. In Arkansas, stripping is done by draglines, shovels, and Carryalls. Stripping ratios of as much as 10 feet of overburden to 1 foot of ore are minable and a ratio of 15 to 1 is considered feasible. Several pits in Arkansas have been mined to depths of more than 100 feet, and about 200 feet is estimated to be the present economic limit for large ore bodies. The pits stand well for unconsolidated rocks, but slumping does occur. Deeper flat-lying ore is recovered at Reynolds Mining Co. Hurricane Creek mine in Arkansas by an underground method of room-and-pillar mining along a retreating cave line. Development is advanced, on a diamond-shaped pattern to the ore limits or caved area and a retreating cave line is induced by systematic pillar recovery closely following room excavation (*34*).

All efforts are made not to leave any unmined ore inside the cave line to avoid excessive pressure on unmined blocks of ore. The caved ground is kept from diluting the broken ore by timbered retaining walls. A cap of about 2 feet of bauxite is left to help support the overlying weak unconsolidated clays and sandstones.

In Jamaica the bauxite deposits lie close to the surface and the overburden of vegetation and topsoil is easily stripped (*13*). The ore is broken by drilling and blasting or by the use of rippers. Shovels, draglines and scrappers are used to load the ore. Haulage is by truck, railroad or aerial tram line to the dryers or alumina plants near port facilities. In Surinam as much as 80 feet is stripped by draglines, hydraulic giants, or dredges. The same methods are used in British Guiana to remove the overburden. The ore is broken by blasting and loaded into ore cars with power shovels (*23*).

Underground mining accounts for more than 80 percent of French bauxite production and is widely used in other parts of Europe including the U.S.S.R. European deposits frequently are in steeply folded limestone beds, and the ore-shoot pattern is typical of sinkhole deposition. Room-and-pillar or shrinkage stoping is used depending on size, dip of the ore body, and condition of the ground.

Restoration of mined-out open-pit areas to usefulness is required in Jamaica and is becoming increasingly important in other areas. Subsidence where bauxite was extracted underground is of minor importance today but may become more serious in the future.

Beneficiation

Bauxite is often washed to remove silica or clay minerals. The high-iron ores of Surinam are concentrated by jigging or heavy-medium separation.

In submarginal bauxites the iron oxides, clay minerals, and part of the titanium minerals are often so finely dispersed through the ore that physical methods have not produced successful separations.

During World War II a pilot plant was operated by the Bureau of Mines at Bauxite, Ark., to test various ore-dressing procedures, including gravity, flotation, and magnetic methods (*30*). Beneficiation by magnetic techniques to eliminate iron is practiced on a limited scale on bauxite for nonmetallurgical uses (*6*).

Processing

Although research on the extraction of alumina has continued for many years, virtually all of the commercially produced alumina is obtained by a process patented by Karl Bayer in 1888 (German Patent 43,977) for use on bauxite. A number of modifications and improvements have been made in the process to adapt it to various types of bauxite. The process involves a caustic leach at elevated temperature and pressure, followed by separation of the resulting sodium aluminate solution, and selective precipitation of the alumina. There are two principal variations of the Bayer process: (1) The European Bayer, in which the approximate conditions of leaching are a pressure of 210 pounds per square inch, a temperature of 390° F, a caustic concentration of 400 grams per liter, and a digestion time of 2 to 8 hours to effect solution of the monohydrate mineral boehmite and (2) the American Bayer, in which a pressure of about 60 pound per square inch, a temperature of about 290° F, a caustic concentration of 170

grams per liter, and a digestion time of one-half to 1 hour are used to dissolve the trihydrate mineral gibbsite (*1*, *25*). The American process is used for treating trihydrate bauxites, because it requires less evaporation and lower temperatures and is more adaptable to continuous digestion.

In both processes the pregnant solution is separated from the red mud tailings by countercurrent decantation and filtration. The liquor is cooled until it becomes supersaturated, then seeded with crystals of aluminum trihydrate. About one-half of the alumina in solution is precipitated in a 36- to 96-hour period. The precipitate is then filtered, washed, and calcined at 2,000° F to obtain the final product. Caustic soda is regenerated in the precipitation step and, together with the unprecipitated alumina, is recycled to the digesters. For some nonmetal uses the alumina is left in the trihydrate form or is only partly calcined.

The finely divided residue resulting from leaching contains Fe_2O_3, TiO_2, and a complex sodium aluminum silicate compound. This compound represents a loss of soda and alumina, and the quantity discarded in the residue is related to the silica content of the bauxite. Approximately 1.1 units of alumina and 1.2 units of soda are lost for each unit of silica in the ore. Bauxite must contain less than 8 percent silica for economic treatment by the Bayer process.

Approximately 4 long dry tons of bauxite is required to produce 2 short tons of alumina, which will yield upon electrolysis slightly more than 1 short ton of aluminum. The materials other than bauxite required in the Bayer process are soda ash; lime for causticizing the soda ash; and fuel oil, gas, or coal.

Crude bauxite from the mines usually is crushed to about 2-inch size in hammermills, gyratories, or jaw crushers. Free moisture, but not the water of crystallization, is removed from the ores by drying when they are to be transported appreciable distances. Bauxite from Surinam and British Guiana is dried to less than 3 percent free moisture. Bauxite from Jamaica and Haiti, after drying, may still contain as much as 15 percent free moisture to prevent dusting when the ore is transported. Further treatment depends upon the end use. Ores for refractory uses are calcined in rotary kilns at 2,500° to 2,900° F and for abrasive uses at 1,700° to 2,400° F to remove water of crystallization.

Bauxite with more than 8 percent silica is treated by the combination process (*3*), which first became commercial as a result of the reduced supply of imported high-grade bauxite during World War II. In this process, bauxite containing 12 to 15 percent silica is first subjected to a Bayer leach. The resulting red mud, which contains the complex sodium aluminum silicate compound, is sintered with limestone and soda ash, then leached with water to recover alumina and soda. The brown mud residue has a composition, on a dry basis, somewhat similar to that of portland cement.

The additional cost required in capital investment, raw materials, and processing by the combination method is partly offset by higher recoveries of alumina and soda and partly by lower mining costs. A major advantage of the combination process is the decreased need for selective mining, as high-silica bauxite, previously regarded as unsuitable for alumina production, can be used. The upper limit of silica for use in this process is now about 15 percent; however, in practice, bauxite containing as high as 25 percent silica is mined and blended with low-silica ore in proportions that will give a feed material of approximately 12 to 13 percent silica. The combination process is used in the two plants in Arkansas and in plants in the U.S.S.R.

In 1952 the American Bayer process was modified to treat the high-iron, low-silica bauxite of Jamaica. The major modifications resulted from difficulties in filtration of the red mud slurry and from the small amount of boehmite in the ore.

In the U.S.S.R., alumina is extracted from nephelite flotation concentrate containing about 30 percent alumina, obtained as a byproduct of apatite from deposits in the Kola Peninsula. The process used is a variation of the lime-soda sinter method, but no soda is added as it is already present in the feed.

In Norway alumina is extracted commercially from high-iron bauxites by the Pedersen smelting process. In this process, bauxite, limestone, coke and iron ore are smelted in an electric furnace to produce pig iron and a calcium aluminate slag containing 30 to 50 percent alumina. The slag is leached with sodium carbonate solution, and the alumina trihydrate is precipitated by carbon dioxide. During World War II the process was also used at a Swedish plant to treat andalusite.

USES

More than 90 percent of the bauxite consumed in the United States is used to make alumina. Less than 10 percent is applied to other uses such as abrasive, refractory, and chemical including aluminum sulfate and other aluminous chemicals used in water and sewage treatment, dyeing, tanning leather, and sizing paper. Bauxite is also used in the production of high alumina cement, in low density insulating materials, as an adsorbent or catalyst by the oil industry, and

as a flux in making steel and ferroalloys. Fused bauxite is used in bonded or coated abrasives or as abrasive grain.

About 94 percent of the alumina production is consumed by the aluminum industry. Alumina also is used for abrasive, refractory, or chemical applications in which a high degree of purity is desirable. Its minor uses include production of the nose cones of missiles, artificial sapphires, and thread guides for textile plants.

BYPRODUCTS

Most bauxites contain small quantities of gallium and vanadium, which dissolve in the Bayer process liquors. Gallium is recovered in the United States by one company, and vanadium is recovered in a French operation. In Norway, iron is produced as a byproduct of the Pedersen process. In the U.S.S.R., potash, soda, and cement are produced as byproducts in recovering alumina from nepheline syenite.

RESERVES

The world bauxite reserve of about 5.7 billion tons and potential resource of about 8.7 tons shown in table 2 were estimated in 1963 by the U.S. Geological Survey. In addition to the countries shown, bauxite also was reported to occur in Poland, Mali and Upper Volta, Portuguese Guinea, Republic of the Congo, Tanzania, North Viet-Nam, and Pakistan (*24*).

Estimates of world bauxite reserves increased 79 percent or an average of about 12 percent per year since 1958 and potential resources increased 46 percent or an average of about 8 percent per year. Australia and Guinea with 57 percent of the world bauxite reserve accounted for most of the increase in reserves. Most of the increase in potential resources was contributed by Australia and Cameroons.

In 1963 the U.S. bauxite reserves totaled 50 million tons averaging about 52 percent Al_2O_3 and 10 percent SiO_2. Of this, 98 percent is in Arkansas and 2 percent in Georgia and Alabama.

The potential bauxite resources shown in table 2 are deposits too low in grade, too deep, too thin, or too remote for profitable recovery under present conditions. The potential bauxite resource, associated with the bauxite reserve in Arkansas, is estimated at 65 million tons. About 25 million tons of low-grade gibbsitic bauxite containing substantial amounts of kaolinite are reported in the Southeastern States. Lower grade ferruginous bauxite deposits in Washington and Oregon formed by weathering of basalt are estimated at 85 million tons. The potential resource in Hawaii is 125 million tons of low-grade bauxite in soils and saprolite weathered from basalt (*8*).

Vast amounts of inorganic materials composed of anorthosite, kyanite, nepheline syenite, alunite, audalusite, and other clays, shales, and slates containing less than 32 percent Al_2O_3 extend over the surface of the earth. These are not included in table 2 but may eventually become a potential resource.

TABLE 2.—*Estimate of world bauxite reserves and potential resources, December 1963 (24)*[1]

[Million tons]

Country	Reserves[2]	Potential
North America:		
United States	50	300
Jamaica	600	400
Dominican Republic and Haiti	85	40
Costa Rica and Panama		80
Total	735	820
South America:		
British Guiana	150	1,000
Surinam	250	150
French Guiana		70
Brazil and Venezuela	40	300
Total	440	1,520
Europe:		
France	70	190
Italy	25	
Yugoslavia	290	
Greece	85	
Hungary	300	100
U.S.S.R.	100	
Rumania, Austria, Spain, and Norway	30	30
Total	900	320
Africa:		
Republic of Guinea	1,100	2,400
Ghana	250	
Cameroon		980
Nyasaland		60
Malagasy Republic, Mozambique, Morocco, Angola, and Rhodesia		60
Total	1,350	3,500
Asia:		
China (mainland)	150	1,000
India	60	200
Indonesia	25	10
Malaya	10	40
Philippines, Sarawak, Iran, and Turkey	25	120
Total	270	1,370
Oceania:		
Australia	2,060	1,190
Fiji Islands, New Zealand, and Palau Islands	5	20
Total	2,065	1,210
Grand total	5,760	8,740

[1] Most of the estimates are in metric or long tons, dry basis; however some estimates did not designate size of ton, wet or dry.
[2] Mostly measured and indicated reserves that could be used under economic and technological conditions existing in 1963.

SOURCES OF STATISTICAL INFORMATION

Statistical information on stocks and production of alumina and shipments of alumina classified by recipient industry are collected annually by the Bureau of Mines. The Bureau

also collects data on the consumption of alumina by the aluminum industry.

Statistical information on domestic bauxite is collected and published periodically by the Bureau of Mines and the Bureau of the Census. Other sources of information include special studies presented in the technical press, reports of aluminum producers and investment companies, and reports by other agencies such as the Federal or State Geological Surveys. The Bureau of Mines publishes quarterly reports and a comprehensive annual report.

Information on foreign bauxite consumption is almost wholly lacking, and data on alumina production and trade in foreign countries are incomplete.

PRODUCTION, CONSUMPTION, AND TRADE

Table 3 shows domestic alumina production and shipments to consuming industries by producers. From 1959 through 1963 shipments to the aluminum industry represented 94 percent of the total shipments. In 1963 exports of alumina were about 10 percent more than imports. Each represented about 4 percent of the total alumina consumed in the United States.

U.S. production, imports, and consumption of bauxite are shown in tables 4 and 5 and world production in table 6.

Exports of bauxite, 1959–63, on a dried-bauxite equivalent basis, ranged from 30,000 to 401,000 tons, averaging about 205,000 tons per year. Of the total exports during this 5-year period 66 percent was exported to Canada and part was returned to the United States as abrasives.

The duties on crude bauxite, calcined bauxite, and alumina imported for making aluminum were suspended until July 7, 1966. Duties on aluminum hydroxide and alumina not used for aluminum production were 0.25 cent per pound.

TABLE 3.—*Production and shipments of alumina in the United States, calcined equivalent*

[Thousand short tons]

Year	Production	Shipments		
		For aluminum	For other	Total
1954–58 (average)	3,252	3,055	147	3,202
1959	4,008	3,765	251	4,016
1960	4,026	3,790	228	4,018
1961	3,844	3,635	232	3,867
1962	4,575	4,244	248	4,492
1963	4,987	4,752	283	5,035

TABLE 4.—*United States supply and self-sufficiency of bauxite*

[Thousand long tons unless otherwise specified]

Year	Domestic production (dry basis)	Imports (crude and dried) [1]						Percent, self-sufficiency
		British Guiana	Dominican Republic	Haiti	Jamaica	Surinam	Other	Total	
1954–58 (average)	1,651	260		127	3,008	2,710	6	6,111	21
1959	1,700	160	384	307	4,220	3,078	0	8,149	17
1960	1,998	330	632	341	4,175	3,256	5	8,739	19
1961	1,228	319	722	289	4,933	2,912	31	9,206	12
1962	1,369	560	719	437	5,986	2,858	15	10,575	11
1963	1,525	335	729	328	5,239	2,518	21	9,170	14

[1] Import figures for Jamaican, Haitian, and Dominican Republic bauxite adjusted by Bureau of Mines to dry equivalent by deducting 13.6 percent free moisture for Jamaican, 14.6 percent for Haitian bauxite in 1957 and 13.6 percent in 1958 and later, and 17.7 percent for Dominican Republic. Other imports, which are virtually all dried, are on an as-shipped basis. Includes bauxite imported for Government account.

Source: Bureau of the Census.

TABLE 5.—*United States consumption of bauxite by industries*

[Thousand long tons unless otherwise specified]

	1954–58 (average)	1959	1960	1961	1962	1963	
						Quantity	Percent
Alumina	6,571	8,027	8,141	8,034	9,878	10,596	93.6
Abrasive	280	217	284	188	261	230	2.0
Chemical	67	238	303	234	244	249	2.2
Refractory	190	82	94	112	138	179	1.6
Other	59	55	61	53	56	64	.6
Total	7,167	8,619	8,883	8,621	10,577	11,318	100.0
Bauxite consumed in aluminum production, percent	84.3	87	87	88	83	82	

TABLE 6.—*World production of bauxite* [1]

[Thousand long tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963
Jamaica	3,630	5,125	5,745	6,663	7,495	6,903
U.S.S.R.[2]	2,180	3,000	3,500	4,000	4,200	4,300
Surinam	3,215	3,376	3,400	3,351	3,202	3,427
British Guiana	2,203	1,674	2,471	2,374	[3] 2,690	[3] 2,210
France	1,528	1,729	2,035	2,190	2,124	1,971
United States	1,651	1,700	1,998	1,228	1,369	1,525
Guinea, Republic of	412	296	1,171	1,739	[3] 1,420	[3] 1,475
Hungary	1,053	923	1,171	1,344	1,450	1,340
Greece	638	904	870	1,100	1,300	[3] 1,280
Yugoslavia	783	802	1,009	1,213	1,311	1,265
Dominican Republic		759	678	739	706	[3] 729
India	102	215	381	468	564	556
Indonesia	261	381	389	413	484	485
Malaya	248	382	452	410	349	444
China (diasporic) [2]	[4] 150	300	350	400	400	400
Australia	8	15	69	16	30	350
Haiti	[5] 272	255	268	263	370	327
Italy	287	290	310	318	304	265
Ghana (exports)	162	148	224	196	287	207
Sarawak	[4] 136	207	285	253	225	155
Brazil	54	95	119	110	188	125
Other countries	[6] 88	112	126	101	65	96
World total (estimate)	19,000	23,000	27,000	30,000	30,000	30,000

[1] This table incorporates some revisions. Data do not add exactly to totals shown because of rounding where estimated figures are included in the detail.
[2] Estimate.
[3] United States imports.
[4] One year only as 1958 was the first year of commercial production.
[5] Average annual production 1957–58.
[6] Average annual production in Pakistan 1955–58.

STRATEGIC CONSIDERATIONS

Previous to 1958 domestic production of alumina met practically all United States requirements. However, in 1958 a U.S. aluminum producer with a capacity of about 54,000 tons, began importing alumina from Japan.

Table 4 shows United States self-sufficiency in bauxite for recent years. The domestic reserve of bauxite is sufficient to maintain an annual production of approximately 1.5 million tons for several decades; the increasing demand must be supplied by imports until production of alumina from domestic low-grade alumina-bearing raw materials, becomes competitive with production from imported bauxite.

Government-owned stocks of bauxite held by Office of Metals Reserve were declared surplus on June 30, 1946, and transferred to the Bureau of Federal Supply and were maintained as the national strategic stockpile. Government inventories on June 30, 1964 are shown in table 7. In addition stocks of refractory grade, calcined bauxite were 300,000 long tons and crude fused and abrasive grain alumina were 400,000 short dry tons.

GOVERNMENT PROGRAMS

During World War II alumina plants were built by the Government to meet the requirements of the aluminum industry. Bauxite reserves in the United States were more than doubled as a result of an extensive exploration program undertaken by the Federal Government and industry. Other Government programs assisted the sharp expansion in domestic bauxite production from less than 500,000 tons in 1940 to the record high of about 6 million tons (dry equivalent) in 1943 and dropping to less than 1 million tons in 1945. Since then production has averaged about 1.5 million tons per year.

During Korean hostilities mining operations in Jamaica and Surinam were increased with U.S. Government assistance. The construction of domestic aluminum plants was encouraged through issuance of accelerated tax amortization certificates and guaranteed market contracts for aluminum.

With the expanding production of aluminum in the United States and the limited reserves of domestic bauxite the Bureau of Mines inaugurated a program to ascertain the technology required to produce alumina from alumina-bearing raw materials. A series of reports have been published on process evaluations to determine the relative processing costs of producing metallurgical-grade alumina from low-grade aluminous materials. The reports include recommendations for additional research and development to improve the processes and to lower their costs (*26–29*).

TABLE 7.—*Bauxite in Government inventories*

[Thousand long dry tons]

Metal grade	National (strategic) stockpile	DPA stocks	CCC stocks	Supplemental stockpile	Total
Jamaica type	880	1,370	805	5,781	8,836
Surinam type	4,963			2,927	7,890

PRICES AND COSTS

Most bauxite is either consumed by the producing companies and their affiliates or purchased under long-term contracts without an open-market price.

Prices per long ton quoted in E&MJ Metal and Mineral Markets for imported bauxite at yearend in 1962 and 1963 were as follows:

	British Guiana f.o.b. port, Dec. 31, 1962	*Atlantic ports f.o.b. cars, Dec. 30, 1963*
Calcined, crushed (abrasive grade)	[1] $21.45	[2] $25.50–$27.50
Refractory grade	27.85	[3] 34.75
Dried bauxite, crushed, chemical grade (60 percent Al_2O_3, 6 percent silica, 1¼ percent iron)	[4] 7.25	13.95

[1] 86 percent minimum Al_2O_3.
[2] 87 percent minimum Al_2O_3.
[3] 87 percent minimum Al_2O_3.
[4] F.o.b. vessels.

The value of shipments of alumina and bauxite as reported by producers is shown in table 8.

TABLE 8.—*Average values of bauxite and calcined alumina*

Year	Bauxite, per long dry ton		Calcined alumina per short ton [3]
	Domestic [1]	Imported [2]	
1954–58 (average)	8.69	8.01	63.56
1959	10.43	9.03	66.80
1960	10.56	8.93	69.80
1961	11.35	9.65	68.80
1962	11.40	11.53	67.20
1963	11.30	12.44	65.20

[1] Average value of mine production.
[2] At port of shipment, as reported to the Bureau of the Census.
[3] Average value of shipments.

TAXES

A State severance tax of $0.10 per short wet ton is levied on bauxite mined in Arkansas. Domestic producers are granted a depletion allowance of 23 percent on income from domestic production and 15 percent on income from foreign production.

The total income from taxes and royalties on exported bauxite and alumina received by the Jamaican Government in 1962 was about $20 million. Exports in 1962 were 6 million tons of bauxite valued at $44 million and 630,000 tons of alumina valued at $40 million or a total bauxite equivalent of 7.4 million tons (dry weight).

Royalties in Surinam are 5 percent or less of the gross value of the product. In 1962 the Surinam Government reported receipts of $5.3 million as royalties and taxes on 3.3 million tons of exported bauxite.

TRANSPORTATION

About 85 percent of the bauxite consumed in the United States is transported from Caribbean islands and the north coast of South America. Ore mined in Surinam and British Guiana is transported from the mines near a river by barge or river vessel to processing plants near the coast. The bauxite is either dried or processed into alumina before loading onto ocean-going ships. Ships leaving British Guiana are lightly loaded to clear an offshore reef. Bauxite-loaded ships are topped at Chaquaramas, Trinidad, and those loaded with alumina are topped at Esquivel, Jamaica.

In Jamaica the bauxite is trucked to railroad loading ramps and transported by gondola cars to drying kilns or alumina plants located at seaports. Some of the bauxite processed at one of the two alumina plants is transported from the mine by aerial tram. The dried bauxite and alumina are loaded onto ore boats of up to 37,600-ton capacity for shipment.

The bauxite and alumina assigned for consumption in the United States is transported to Gulf ports where most of the bauxite is processed into alumina. Nearly all of the domestically processed alumina and the imported alumina and some of the imported bauxite is shipped by railroad cars, barges, trucks and ocean going ships to aluminum plants and other alumina-consuming industries.

Some alumina is transported by ship from Japan to the west coast. Alumina produced in Jamaica and the gulf coast area of the United States is transported by ship through the Panama Canal to aluminum producers in the Northwestern United States and Kitimat, British Columbia.

RESEARCH

During World War II an extensive research program aimed at developing methods for recovering alumina from low-grade ores was undertaken by the Bureau of Mines. Methods for upgrading low-grade bauxites (those with high-silica and/or high-iron content) were investigated. Acid and alkaline processes for extracting alumina were tested and the most promising methods investigated on a pilot-plant scale. During this period other Government and private organizations conducted research on similar processes.

Recent Bureau of Mines research included studies of recovery of alumina from anorthosite by the lime-soda-sinter process (*19*, *20*, *29*, *31*). Studies on properties of aluminum nitride and preparation of aluminum fluoride were investigated (*2*, *18*, *21*).

The Bureau also conducted cost evaluations for the production of metallurgical-grade alumina from low-grade aluminous materials using sulfuric acid, hydrochloric acid, and potassium alum processes (*26–29*). Metallurgical investigations were conducted for recovery of alumina from ferruginous bauxites (*4*, *17*).

All eight companies producing aluminum have laboratories in which research is in progress on improving present processes for recovering alumina from noncommercial materials. The Anaconda Company continued to operate a 5-ton-per-day pilotplant at Anaconda, Mont., for the production of alumina from high-alumina clay using hydrochloric acid. During part of 1962–63, the North American Coal Corp. produced a high-grade aluminum sulfate from coal shale at Powhatan, Ohio. In West Germany a vacuum crystallization technique with sulfuric acid was used to separate aluminum sulfate from iron. Pure alumina was produced experimentally by hydrolysis and alkaline treatment of aluminum sulfide slag.

Hydrolysis was also used to form a basic alumium sulfate (*32*).

In addition, studies at some laboratories were directed toward expanding the use of alumina by refractory, abrasive, petroleum, and other industries.

OUTLOOK

Based on past records and the normal patterns of bauxite use, U.S. consumption is expected to continue to increase between 7 and 8 percent per year during the next 10 to 20 years, and more than 90 percent will be used in the preparation of aluminum metal. At this rate bauxite consumption in the United States would reach about 19 million tons per year by 1970 and 40 million tons by 1980. However, if the tendency to construct alumina plants closer to the sources of bauxite, which has been evident in recent years continues, demand in the United States will not reach this high level. An equivalent quantity of Al_2O_3 probably will still be required.

Domestic production of bauxite is expected to remain at the present rate of about 1.5 million tons per year for the next decade. Increased bauxite requirements will be met by imports. Foreign sources supplied 86 percent of the bauxite consumed in the United States in 1963 and by 1970 they are expected to supply 92 percent.

U.S. imports from Surinam will probably remain relatively constant at about 3 million tons per year. Jamaica, which supplies about half of the bauxite used in the United States, is expanding production and should supply most of the additional bauxite needed.

Bauxite containing in excess of 40 percent alumina will remain the primary raw material source of alumina for the immediate future and the Bayer process is likely to continue to be the principal method for the extraction of alumina from bauxite. By the 1980's it is possible that the industry will begin to process low-grade domestic bauxites, clays, or other materials such as alunite, anorthosite, and leucite containing as little as 30 percent alumina as raw materials for aluminum production.

Total requirements for commercial-grade metallurgical bauxite will be approximately 4 times by weight the quantity of primary metal produced. A decrease in this ratio may take place if processes are developed to reduce aluminum metal directly from the ore, thereby eliminating the intermediate alumina stage.

Alumina used in refractory, abrasive, and chemical applications should continue to use slightly less than 10 percent of the total alumina consumed in the United States. Inherent desirable mechanical and electrical characteristics of alumina should lead to new and expanded uses in missiles and complex electronic systems.

The world production rate for bauxite should parallel that for U.S. consumption. Using about the same growth rate world production of bauxite would reach 50 million tons per year by 1970 and 100 million by 1980.

PROBLEMS

One of the most serious problems confronting the domestic alumina producers is that of acquiring adequate and dependable alternate sources of alumina-bearing materials for the continued use of an expanding industry and freeing the industry from uncertain foreign suppliers. This problem is further enlarged by the foreign governments which plan to improve their economy by processing indigenous minerals to a more advanced state. Thus, in order to secure mineral rights the investing company often must also build an alumina plant, a smelter, and special facilities including electric powerplants within the country.

The domestic bauxite mining industry is faced with the problem of high cost of mining small and underground deposits. Another problem is lack of a rapid method of analysis for alumina to help plan direction of mining and to better control selective mining to obtain a more uniform product and use more low-grade ores. Large-scale open-pit operations are confronted with growing demands for surface restoration. Improvements in transportation are needed to lower the costs of shipping ore and alumina.

Detailed information on the location, extent, grade, and nature of potential resources of aluminum is needed in formulating long-range plans for commercial development of such resources. In addition more research is needed to develop suitable processes for producing alumina from domestic low-grade aluminous materials. Technical problems include the elimination of iron and silica, prevention of gelation of alkaline slurries, lack of stability of alkaline alumina solutions, the need for low-cost acid-resistant construction materials, and the lack of precise knowledge of chemical reactions involved.

Problems in improving the Bayer and combination processes include process inefficiencies related to preparation of ore and digestion conditions, removal of soluble impurities and solids, decomposition of sodium aluminate solutions, calcination of aluminum hydrate, scale-forming tendencies of the liquor in the thickeners, and utilization or disposal of increasing quantities of red mud tailings from plant operations.

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ALUMINUM[1]

By John W. Stamper[2]

GROWTH of the primary aluminum industry in the United States has been so rapid that the quantity produced annually now exceeds that of any other nonferrous metal. Since 1955 aluminum production in the United States has exceeded 1.5 million tons annually. Aluminum is of great importance in the aircraft industry, and efficient, competitive operation of many other industries requires a continued supply of the light metal.

The basic process for producing aluminum, developed independently by Hall and Héroult nearly 75 years ago, is by electrolysis of high-purity aluminum oxide in a bath of molten cryolite. Research in reduction cell design and development of larger cells has led to economies in power and manpower requirements. There has been much research on other processes for recovery of the metal, but none has proved more economical.

Except for a few years immediately before World War II the United States has been the world's leading producer of aluminum and accounted for 38 percent of world output in 1963. The output of the U.S.S.R., the second largest producer, represented an additional 17 percent of the total. For the past 10 years U.S. imports have accounted for an average of 11 percent of the total supply of crude and scrap aluminum; and 85 percent of the bauxite used in 1963 was imported.

The recovery of secondary aluminum, from 1959 to 1963, averaged 19 percent of the apparent consumption of primary and secondary aluminum recoverd. New scrap is the source of 80 percent of the secondary metal recovered.

The primary aluminum industry expanded sharply under the impetus of World War II and the Korean war—partly with the aid of Government funds and incentives. In 1940, there was one domestic primary aluminum producer, by 1963 there were seven, three of which were completely integrated from the mine to aluminum fabricating plants. Much of the primary production is consumed in semifabricating plants owned by the producers.

Since approximately 20 percent of the cost of aluminum is electric energy, the aluminum industry, has until relatively recent times, built plants near sources of low-cost hydroelectric power. However, since World War II, demand for power in industrially developed countries has increased sharply and competing industries can pay more than the aluminum industry for power. The domestic aluminum industry turned first to hydroelectric power, second to natural gas, then to lignite, and in 1957 new aluminum smelters were built near large coal deposits. Aluminum producers in many foreign countries have constructed plants in relatively isolated and thinly populated areas where hydroelectric power could be made available.

The progressive research, development, and sales policies of the aluminum producers have resulted in the displacement of many materials from their historical market by aluminum. The relatively stable price of aluminum has been an important factor in the increased usage of the metal. Industries which consume major quantities of aluminum are—Building and construction, transportation, consumer durables, containers and packaging, electrical equipment, and machinery and equipment. As applications for aluminum are developed and current markets are expanded, production and consumption of this versatile metal are expected to continue to expand at a greater rate than the national economy.

Maintenance of an adequate aluminum supply requires assured sources of alumina and electrical energy. Continuation of research on reactions in the electrolytic cell may result in a decrease in power and manpower requirements. Alloy and product research will lead to the development of new uses that will consume large quantities of aluminum.

[1] Alumina, bauxite, and recovery of alumina are discussed in the Alumina and Bauxite chapter.
[2] Commodity specialist.

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BACKGROUND

Recognizing that alumina was the oxide of a metal, Sir Humphry Davy, in 1808, named the metal "alumium" which he later changed to "aluminum." Later the spelling "aluminium" came into general use and is still used in many countries. In the United States the simpler spelling "aluminum" was adopted.

Davy's attempts to isolate the metal were unsuccessful, but in 1825 Hans Christian Oersted produced aluminum by treating aluminum chloride with potassium amalgam. Frederick Woehler, some years later, produced an impure powdered aluminum using potassium as the reducing agent. Henri Ste. Claire Deville, in France, using sodium metal as the reducing agent, produced the first commercial quantities of aluminum in 1854. Although much research was done on lowering the cost of the sodium, aluminum was never produced by this method at a price competitive with other nonferrous metals. In 1857 aluminum was $27 per pound and the price was reduced to $17 by 1859.

In 1885 less than 300 pounds of aluminum was produced in the United States, but the discovery of an electrolytic process in 1886 by Charles Martin Hall in the United States and independently by Paul Héroult in France opened the way for a new industry. Using this new process, by 1895 production had increased to 900,000 pounds and prices had decreased from $10 to $0.59 per pound. Now, over 75 years following the discovery of the process, equipment has undergone substantial change and refinement, but the Hall-Héroult electrolytic process still is used. In 1963, when primary aluminum production was more than 2.3 million tons, the price of ingot averaged 22.6 cents a pound.

Beginning in 1954 and continuing through 1963, production of primary aluminum in the United States has exceeded that of any other nonferrous metal. The United States has been the world's leading aluminum producer except during 1934–1940, when for 5 years Germany was the leading producer. Since 1942 Canada has been the second largest producer in the free world. Estimates of production in the U.S.S.R. indicate that country has become the second largest producer in the world since 1958.

The Aluminum Company of America (Alcoa), owning bauxite, alumina, and aluminum producing facilities, was the only domestic producer from 1886 to 1940. Under the impetus of World War II, domestic aluminum capacity was expanded sharply and by 1946, two additional producers, Reynolds Metal Co. and Kaiser Aluminum & Chemical Corp., had entered the field. In 1954, the Anaconda Aluminum Co. began producing primary aluminum. In 1958, Harvey Aluminum, Inc., and Ormet Corp. (a subsidiary of Olin Mathieson Chemical Corp. and Revere Copper and Brass, Inc.) became producers of primary metal. The latest entrant in the field, Consolidated Aluminum Corp. (Conalco), a fully-owned subsidiary of Swiss Aluminum, Ltd., Zurich, Switzerland, started production of primary aluminum in 1963.

SIZE AND ORGANIZATION OF THE INDUSTRY

Figure 1 of the Alumina and Bauxite chapter illustrates the organization of the domestic industry and shows primary aluminum plant locations and capacities (including plants under construction). Data in table 1 summarize information on productive aluminum capacity existing at the end of 1963.

TABLE 1.—*Primary aluminum productive capacity, Dec. 31, 1963*

Company	Number of aluminum production plants	Annual capacity, thousand short tons
Aluminum Company of America	8	853
Reynolds Metals Co	7	701
Kaiser Aluminum & Chemical Corp	4	609
Ormet Corp	1	180
Harvey Aluminum Co	1	80
Anaconda Aluminum Co	1	68
Consolidated Aluminum Corp	1	20
Total	23	2,511

Three of the seven primary producers, with 86 percent of U.S. productive capacity at the end of 1963, were vertically integrated from mining through production of semifabricated shapes. The remaining firms also had facilities for producing semifabricated shapes. About 80 percent of the domestic production of primary aluminum is used by these 7 firms or exported. Independent producers of semifabricated shapes and affiliates of foreign producers of primary metal use most of the aluminum imported into the United States.

Data on world capacity to produce primary aluminum in table 2 show that during 1958–63 the primary aluminum industry grew much faster in foreign countries than in the United States and Canada.

Reduction plants owned or partially owned by governments, representing about 9 percent of the free world productive capacity for primary aluminum, are operated in West Germany, Norway, Spain, Yugoslavia, Taiwan, and Austria. About 80 percent of the free world productive capacity in 1963 was operated by subsidiaries or affiliates of six corporate groups: Aluminium Ltd. and its subsidiary, the Aluminum Company of Canada, Ltd. (Alcan), Reynolds, Kaiser, the two associate French companies, Péchiney-Ugine (Péchiney Compagnie de Produits Chimiques et Electrometallurgiques and Société d'Electro-Chimie, d'Electro Metallurgie et des Aciéries Electriques d'Ugine), and Swiss Aluminium, Ltd.

TABLE 2.—*World primary aluminum productive capacity, Dec. 31, 1958 and 1963*

Country or continent	Annual capacity, thousand tons		Percent increase
	1958	1963	
United States	2,194	2,511	14
Communist countries	846	1,415	67
Europe	767	1,318	72
Canada	865	905	5
Asia	106	371	250
Other countries, including South America, Africa, Australia, and Mexico	76	219	188
Total	4,854	6,739	39

In 1963, U.S. companies owned primary aluminum plants in foreign countries, or were affiliated with firms which operated primary aluminum plants in foreign countries, having about 10 percent of the productive capacity in the free world, exclusive of the United States. U.S. companies also owned or partially owned various processing facilities in foreign countries. A Swiss company owned a primary aluminum plant in the United States and several foreign primary producers owned or were affiliated with producers of various aluminum products in the United States.

GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

The aluminum reduction industry is a major consumer of electric power and uses approximately 3 percent of the domestic electric power generated. To maintain its competitive position, large quantities of low cost dependable electrical energy are a necessity for this industry. Before 1950 plants were built near sources of low-cost hydroelectric power such as the Niagara Falls area, the Tennessee Valley area, and the lower Columbia River area of the Pacific Northwest. However, aluminum consuming and other industries entered these areas, and in some instances the cost of power from new facilities was increased. Since 1950, in addition to situating plants in the limited number of places where new hydropower supplies became available, the industry has built several large plants where natural gas, lignite, or bituminous coal for thermally generated electric power are available.

As indicated by figure 1, of the Alumina and Bauxite chapter, the raw material for the primary aluminum smelters, is produced in the South Central United States in Arkansas, Texas, Louisiana, and Alabama. The reduction plants are more widely dispersed, as shown in table 3.

TABLE 3.—*Geographic distribution of aluminum reduction plants, Dec. 31, 1963*

Location	Number of aluminum reduction plants	Annual capacity, thousand tons	Percent of total
Pacific Northwest	8	722	29
Alabama, Tennessee, and North Carolina	4	414	17
Arkansas and Louisiana	3	412	16
Texas	3	385	15
Ohio, West Virginia, and Indiana	3	360	14
New York	2	218	9
Total	23	2,511	100

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Pig is metal initially produced by a primary reduction plant, taken directly from the reduction cell and cast into a convenient form. Pig is cast in a wide variety of sizes, but the usual commercial size is 50 pounds, with a 99.5 percent guaranteed minimum aluminum content. Use of the term "pig" in the aluminum industry was discontinued in 1960.

Ingot is a cast form suitable for working or remelting that has been poured from either a melting or alloy furnace. A common commercial size is 30 pounds and the aluminum content is 99.5 plus percent. Since 1960 the term "ingot" represents metal that previously was referred to as pig.

Potline is a number of reduction cells or pots, usually 100 to 150, connected in electrical series.

Super-purity aluminum contains a minimum of 99.99 percent aluminum.

Aluminum alloys are generally divided into two major groups: Wrought and casting. Table 4 gives the chemical composition for two alloys of each type. Unalloyed metal usually contains 99.5 percent aluminum and small quantities of iron and silicon. Even when no alloying elements have been added, the quantity of impurities present has to be controlled

carefully. Metal with over 99.5 and up to 99.85 percent aluminum is available at costs up to 3 cents per pound more than standard commercial metal. It is used where superior electrical conductivity or corrosion resistance is required. Purities higher than 99.85 percent are necessary for certain applications.

There are several acceptable methods of designating aluminum alloys. However, a 4-digit code for wrought alloys was adopted by The Aluminum Association in October 1954. The first digit indicates the major alloying ingredient. If the first digit is 1 the alloy has a minimum aluminum content of 99.00 percent. Digits 2 to 8 in the first position designate copper, manganese, silicon, magnesium and silicon, zinc, and other element, respectively; 9 is an unused series.

TABLE 4.—*Chemical analysis of some aluminum alloys, in percent* [1]

Type and number	Cu	Fe	Si	Mn	Mg	Zn	Ti	Cr	Other elements	
									Each	Total
Wrought 1100 [2]	0.20	Fe+Si 1.0		0.05		0.10			0.05	0.15
Wrought 2024	3.8–4.9	0.50	0.50	0.30–0.9	1.2–1.8	.25		0.10	.05	.15
Casting 43	.10	.8	4.5–6.0	.30	0.05	.20	0.20		.05	.15
Casting 108	3.5–4.5	1.0	2.5–3.5	.30	.03	.20	.20			.30

[1] Values are maximum unless shown as a range; aluminum is remainder.
[2] Aluminum minimum—99.00 percent.

If the alloy has a minimum aluminum content of 99.00 percent, the second digit indicates special control on impurities and the last two digits indicate the minimum aluminum content figures to the right of the decimal point. Thus, 1030 indicates 99.30 percent minimum aluminum content without special control on individual impurities.

When the first digit is 2 through 8, indicating a major alloying ingredient, the second digit indicates alloying modifications and the last two digits identify the alloy, usually by the commercial code number previously used to designate the same alloy. Thus, 2014, formerly alloy 14S, contains copper as the major alloying ingredient with no alloy modification.

Additional letters, O and F, and letters H and T with numbers, may follow the alloy digits and designate the temper of the alloy.

No uniform system has been adopted by the industry for designating casting alloys. These alloys may be designated by American Society for Testing and Materials numbers, U.S. Federal Specifications, Society of Automotive Engineers, commercial, and individual company symbols.

TECHNOLOGY

Primary Aluminum (*2, 7, 14, 17*) [3]

Primarily aluminum is produced by the electrolysis of alumina in a molten cryolite bath. Purity of the alumina used must be greater than 99.0 percent. The electrolytic reduction cell consists of a carbon-lined box containing a pad of molten aluminum which serves as the cathode, a carbon anode, and an electrolyte of molten cryolite in which the alumina is dissolved. Small quantities of aluminum fluoride are used in the electrolyte to combine with Na_2O, an impurity in alumina, to form artificial cryolite, and the melting point of the bath is lowered by the addition of small quantities of fluorspar. The anode may be either one large block of carbon or a number of small blocks of carbon. The alumina is reduced to aluminum at the cathode and carbon is oxidized to carbon dioxide at the anode.

The carbon lining, which contains the molten aluminum, is built into a steel shell. Typical dimensions of the shell are 20-feet long, 10-feet wide, and 3-feet deep. It is lined first with refractory insulation. The insulation is then lined with carbon blocks, joined by carbon cement, or a monolithic lining is prepared by baking carbon paste in place. The carbon lining usually must be replaced after 3 to 4 years.

The carbon anodes are consumed at a rate of about 1 inch of vertical length per 24 hours of operation and the method of replacement is important in regard to overall costs. There are two methods of replacing anode carbon through: (1) soderberg continuous anodes and (2) prebaked anodes.

In the Soderberg anode a reinforced rectangular steel shell, open at the top and bottom, is suspended above the furnace. Carbon paste or briquets of coke and pitch are added period-

[3] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

ically as the anode is consumed. Current enters the anode through rows of pins inserted into the carbon mass either vertically or horizontally. The heat of the bath and the heat resulting from the electrical resistance of the carbon bake the paste or melt and bake the briquets so that at a point approximately 20 inches above the bath the carbon becomes a hard monolithic mass. The steel pins, in addition to conducting current, support the carbon mass. As the carbon descends through the hopper and is consumed, the lowest pins are periodically withdrawn and replaced at higher levels in the anode box. The optimum anode-cathode distance is maintained by raising or lowering the pins which are baked into the lower part of the carbon block. Inasmuch as the pad of molten metal builds up at approximately the same rate as the anode is consumed this adjustment is usually made only when metal is withdrawn from the cell.

In the prebaked anode system sets of 16 to 24 prebaked carbon blocks are used. The size of the blocks varies from plant to plant; in one plant the blocks are 20 inches wide, 31 inches long, 12 inches high, and weigh about 400 pounds. The blocks are supported in the bath by steel stubs or rods which conduct the current to the carbon. These stubs are inserted into a hole in the top of the finished block and anchored in place by casting molten iron around the stub. The blocks are raised or lowered separately to maintain proper position with respect to the bath and are replaced individually as they are consumed.

The Soderberg system requires less labor and, with the exception of moving the steel pins, is a continuous method of feeding anode carbon. The prebaked system results in better electrical efficiency in the reduction cell but requires fabricating and rodding facilities not used in the Soderberg system.

The molten bath or electrolyte may be as deep as 14 inches, but the anode is usually only 2 inches from the pad of molten aluminum. The resistance of the bath is sufficient to maintain an optimum operating temperature of 950° to 1,000° C. At this temperature the alumina dissolved in the bath ranges from 6 to 10 percent. When the alumina concentration drops to 2 percent, the electrical resistance of the cell increases sharply and the voltage drop across the cell increases from 5 volts to 30 or 40 volts. The phenomenon is known as the "anode effect." As soon as this condition occurs, the crust of frozen cryolite on top of the bath is broken and more alumina is added to the cell which then returns to normal operating condition.

Every 1 to 3 days the molten aluminum is removed from the cell by aspiration. Cast iron pots with airtight lids and downward sloping spouts are used. The molten metal is blended with other batches and then may be fluxed, alloyed, cast, or if the fabricating facility is nearby, transported molten to the fabricating plant.

Plants constructed since 1950 have much larger cells than were used in older plants. These cells utilize currents from 65,000 to 125,000 amperes, with the majority of plants having 80,000- to 100,000-ampere cells. The voltage drop across a single cell is 4.5 to 5.0 volts and across a potline 600 to 800 volts.

The larger cells require less manpower per pound of aluminum produced, but special problems are encountered in cells designed to use 100,000 and more amperes. The large currents cause powerful magnetic fields in the metal and bath, resulting in violent agitation. This agitation causes a fog of aluminum to be dispersed in the bath which increases the possibility of reversing the reduction reaction. Another detrimental effect is that the molten metal piles up toward the negative leads causing a variation in the anode-cathode spacing. Moreover, localized thermal effects may distort the carbon lining.

Current efficiency ranges from 85 to 90 percent; losses are principally due to physical losses of metal and reoxidation of aluminum by carbon dioxide. Owing to the electrical resistance the voltage efficiency is only 40 percent with heat being lost by radiation, and in the exhaust gases, in tapped metal, and in electrodes removed from the cell. As a result the overall energy efficiency is about 35 percent. About 7 to 8 kilowatt-hours is required in the cell per pound of aluminum metal produced. Total plant requirements are less than 10 kilowatt-hours per pound.

Table 5 summaries the raw materials used in producing 1 pound of aluminum.

TABLE 5.—*Raw materials and energy required to produce 1 pound of aluminum*

	Quantity
Alumina ---- pound	1.93
Cryolite ---- do	0.02–0.03
Aluminum fluoride ---- do	0.02–0.03
Fluorspar ---- do	.003
Anode carbon ---- do	.55
Cathode carbon ---- do	.02
Electrical energy ---- kilowatt-hours	7–8

To prevent pollution of the atmosphere, gases from the cells are passed through a collection system which removes alumina, carbon, and fluorides.

The relatively low tensile strength of commercially pure aluminum limits its use in heavy durable products. However, by alloying, cold rolling, or heat treating, aluminum

alloys with strengths approaching those of mild steels have been developed. There are more than 100 commercially-available aluminum alloys and several new alloys usually are developed each year. The alloys offer a wide variety of combinations of mechanical strength, ductility, electrical conductivity, and corrosion resistance. A small addition of manganese increases the strength of wrought aluminum. Magnesium and silicon, together or separately, give aluminum alloys with good corrosion-resistance and strengths. Copper and zinc are used to produce alloys with high strength-to-weight ratios. Small quantities of other metals such as nickel, chromium, titanium, and tin are sometimes added for grain refinement or to impart special characteristics.

The production of super-purity aluminum requires a second electrolytic step in which a cell, known as the Hoopes cell, with three molten layers is used. The bottom layer is the anode, a relatively impure aluminum alloyed with copper to increase its density. The intermediate layer in the conventional Hoopes cell is molten cryolite with barium fluoride added to give it a density greater than that of pure aluminum. The top layer, which serves as the cathode, is molten super-purity aluminum.

Secondary Aluminum (*3, 13*)

Much aluminum scrap is processed into secondary aluminum ingot without preliminary treatment. New scrap requires little or no sorting, and manual sorting of old scrap is too expensive to be widely practiced. Scrap in the form of borings and turnings is dried and the oil removed by burning. Tramp iron is removed by magnetic separators. Dross and foil also usually require treatment before being melted. From 40 to 95 percent of the scrap is recovered as metal. Low recoveries are obtained from drosses and skimmings; high recoveries from segregated sheet and clips.

Most scrap is melted in 5- to 25-ton capacity reverberatory furnaces operated on a 24-hour cycle. Important advantages of this type of furnace are its ease of mechanical charging, low flux consumption, and a melt loss of only 2 to 5 percent. The molten aluminum is protected from surface air oxidation by a layer of flux, which usually contains sodium chloride, potassium chloride, and cryolite. Other salts which may be included are calcium chloride and sodium fluoride. The melt may be refined by passing chlorine gas through the molden metal or by using reactive salts such as aluminum fluoride or sodium silicofluoride in the flux. Nitrogen is introduced to degas the melt and bring the dross and oxides to the surface.

Some scrap processing plants have dust- and fume-collecting equipment. Electrostatic precipitators and Venturi scrubbers apparently are effective in removing volatile alkali chlorides and fluorides as well as particles of aluminum, magnesium, and silicon from the exhaust gases. In small, intermittent operations, furnaces may be in the open or poorly hooded and therefore can be contributors to air pollution (*1*).

Secondary smelters consuming aluminum scrap produce specification wrought and casting alloys. Casting alloys account for most of their production. Once the scrap has been melted alloying ingredients or primary aluminum are added to bring the melt to specification.

USES

Aluminum is used in many products because of its low density, high electrical or thermal conductivity, resistance to corrosion, low neutron absorption cross-section, nontoxicity, malleability, reflectivity, nonmagnetic and nonsparking properties, or high strength-to-weight ratio. In many applications aluminum is in direct competition with copper, steel, magnesium, lead, wood, plastics, rock wool, or fiberglass.

Shipments of aluminum are usually divided into the following three major categories: (1) wrought products, such as rolled, extruded and forged shapes, (2) cast products, and (3) products for dissipative uses in which the metal loses its identity as in its use as an alloying ingredient in nonaluminum base alloys, a deoxidizer in the production of steel, or in the production of aluminum chemicals. Net shipments, classified as wrought or cast products, are shown in table 6. In addition, about 66,000 tons of ingot was shipped to government stocks in 1962 and 1963 and it is estimated that 100,000 tons has been consumed annually in dissipative uses.

About 25 percent of the aluminum consumed domestically is used for construction in such items as siding, roofing, curtain walls, flashing, insulation, windows and screening, and builders' hardware.

The transportation industry is also a major consumer of aluminum accounting for more than 20 percent of total consumption. The high strength-to-weight ratio of aluminum makes it valuable in any carrier, but this factor has been most important in aircraft. In buses and truck trailers it often accounts for 15 to 40 percent of the total weight of the vehicle. Since 1945, railroad equipment manufacturers have greatly increased their use of aluminum for trim and accessories. A few "all aluminum" passenger and freight cars have been built.

During the 1920's a number of automobiles used large quantities of aluminum, but the price and supply of aluminum were such that as automobile production increased and steel technology improved, the use of aluminum in automobiles gradually decreased until 1946 when only about 7 pounds of aluminum were used per automobile. Since then, this decreasing trend has been reversed. In 1955, an average of 30 pounds per car was used and the 1964 models contain an average of 72 pounds of aluminum per car. Major aluminum components in automobiles are pistons, automatic transmission parts, and trim. In 1963, one automobile manufacturer in the United States was producing a car powered by an engine made largely from aluminum.

TABLE 6.—*Net shipments*[1] *of aluminum wrought and cast products by producers*

[Short tons]

	1962	1963
Wrought products:		
Plate, sheet, and foil	1,004,146	1,161,807
Rolled structural shapes, rod, bar, and wire	260,721	270,828
Extruded shapes, rod, bar, tube blooms, and tubing	579,268	634,681
Powder, flake, and paste	21,841	22,405
Forgings	39,684	42,082
Total	1,905,660	2,131,803
Castings:		
Sand	73,366	72,003
Permanent mold	147,348	149,844
Die	240,717	253,806
Other	(1)	(1)
Total	463,414	[2] 476,399
Grand total	2,369,074	2,608,202

[1] Figure withheld because estimates did not meet publication standards of the Bureau of the Census.
[2] Includes a small quantity of "All other aluminum" castings shipped for sale.

Source: Bureau of the Census.

Only in the past 30 years have marine applications of aluminum become important. During this period alloys with high mechanical strength and high corrosion resistance have been developed, and the problem of bimetallic corrosion has been largely eliminated by proper insulation. Approximately 2,000 tons of aluminum was used in the superstructure, decks and deckhouses, stack enclosures, bulkheads, and lifeboats of the SS *United States*. Many small pleasure craft are fabricated almost entirely from aluminum.

About 10 percent of the total quantity of aluminum consumed goes into consumer durable goods including refrigerators, air conditioners, washing machines, furniture, utensils, and small appliances.

Ten percent of the aluminum consumed is used in the electrical and communications industries. In most instances aluminum cable with steel reinforcing has displaced copper for cross country transmission lines. It is estimated that aluminum conductors account for 90 percent of all new transmission lines in the United States. Aluminum conductor is also used in urban distribution lines and service drops.

Aluminum containers and packaging including foil, caps and closures, and collapsible tubes account for nearly 10 percent of total aluminum consumption.

Its use in machinery and equipment, in the chemical and metallurgical industry, and miscellaneous uses consume approximately 20 percent of the total aluminum supply.

Super-purity aluminum has a number of applications including its use as a catalyst for producing high octane gasoline, as an electrical capacitor foil, and in consumer products such as automobile and appliance trim and costume jewelry.

ALTERNATE MATERIALS

If aluminum supplies were curtailed, or the price increased, steel and stainless steel, magnesium, zinc, titanium, lead, copper, plastics, fiberglass, or wood could be used in place of aluminum in applications where these materials have been used previously. Steel, stainless steel, magnesium, and zinc can be substituted for aluminum in the automotive industry. Magnesium could replace aluminum for certain components in commercial aircraft, and stainless steel and titanium may replace aluminum in jet aircraft. Fiberglass, titanium, and wood may be substituted for aluminum in small boats. Copper could replace aluminum in electrical applications and lead foil or plastics could serve as substitutes in packaging.

The increase in aluminum consumption has resulted, in part, from the decrease in the price of aluminum in relation to other metals. Historically a 1 percent decrease in the ratio of the price of aluminum to the composite price of copper, lead, and zinc has increased aluminum consumption by 1.4 percent.

SECONDARY SOURCES AND RECOVERY

The recovery of secondary aluminum, from 1959 through 1963, as reported to the Bureau of Mines, averaged 19 percent of the apparent consumption of primary and secondary aluminum recovered. The scrap from which secondary aluminum is recovered is designated as either "new scrap" or "old scrap." New scrap is generated from (1) fabricating operations such as alloying, stamping, forging, ex-

truding, machining and casting and (2) rejected semifabricated and manufactured items. Old scrap is aluminum that has been used in end products and is collected for metal recovery after the products are worn out or discarded. New scrap consumption and metal recovery data are based on quantities treated outside of the generating plant and do not include "run-around" scrap consumed in the generating plant.

New scrap is the source of nearly 80 percent of the secondary aluminum recovered. The relatively small recovery from old scrap reflects the fact that the aluminum industry is a new and growing industry. Moreover, the high ratio (4:1) of new to old aluminum scrap shows that old aluminum-containing products are not being replaced as rapidly as new ones are going into use. The tonnage of aluminum in use represents a growing reservoir of old scrap for the future.

Consumers of scrap aluminum are divided into the following four major categories: (1) secondary smelters, (2) primary producers and fabricators, (3) foundries and miscellaneous manufacturers, and (4) chemical plants. The secondary smelters accounted for about 75 percent of the scrap consumed from 1959 through 1963. During this period smelters produced an average of 350,000 tons of secondary aluminum ingot annually. Much of this was consumed in the production of castings.

As indicated by the data in table 7, small quantities of aluminum are recovered from nonaluminum-base alloy scrap and some of the aluminum recovered is consumed in the production of such alloys and also in aluminous chemicals.

TABLE 7.—*Aluminum recovered from scrap processed in the United States, by kind of scrap and form of recovery*

[Short tons]

Kind of scrap	1962	1963	Form of recovery	1962	1963
New scrap:					
Aluminum-base	332, 734	389, 263	As metal	35, 269	25, 114
Copper-base	42	56	Aluminum alloys	423, 725	469, 337
Zinc-base	202	131	In brass and bronze	131	538
Magnesium-base	258	220	In zinc-base alloys	611	5, 121
			In magnesium alloys	292	1, 636
Total	333, 236	389, 670	In chemical compounds	1, 728	3, 845
Old scrap:			Total	461, 756	505, 591
Aluminum-base	127, 756	115, 164			
Copper-base	89	76			
Zinc-base	443	436			
Magnesium-base	232	245			
Total	128, 520	115, 921			
Grand total	461, 756	505, 591			

RESERVES (5)

Reserves and resources of bauxite and other potential aluminum ores are discussed in the "Alumina and Bauxite" chapter.

SOURCES OF STATISTICAL INFORMATION

Data on production, shipment, stocks, and value of primary aluminum are obtained monthly from all domestic producers by the Bureau of Mines. Alumina consumption is obtained annually. The Bureau also canvasses, on a monthly basis, secondary smelters and other scrap consumers to determine stocks and receipts of scrap from which monthly consumption is calculated. Production of ingot by secondary smelters is calculated from their monthly reports of stocks and shipments. Coverage of the secondary aluminum industry is estimated at more than 80 percent. Data on the operations of the members of the Aluminum Smelters Research Institute are obtained from that association. The data on both primary and secondary aluminum are published monthly and annually; the secondary data include an estimate for full coverage of the industry.

The Bureau of the Census collects and publishes monthly data on net shipments of aluminum wrought and cast products. The Bureau of the Census also obtains monthly information on imports and exports of all forms of

aluminum. The 1958 Census of Manufacturers included statistics on employment, materials consumed, electric energy purchased, and expenditures for plant and equipment.

With the exception of 1 year, data on aluminum consumption are incomplete. In 1952, under the Controlled Materials Plan, aluminum suppliers were required to report quantities of metal shipped to different segments of the consuming industries. Since then The Aluminum Association has published, semiannually by percent, shipments of wrought products, sand castings, and permanent mold castings to different major uses, as reported by its members. Although coverage is limited to members of the Association which represent about 80 percent of the wrought products producers and a much smaller part of the casting industry, the breakdown for wrought products and sand castings is believed to be representative of the entire industry.

PRODUCTION, CONSUMPTION, AND TRADE

In 1900, aluminum was produced in only four countries, and output totaled 7,500 tons. In 1963, there were 24 producing countries, and production reached 6.1 million tons as shown in table 9. The United States with a production of 2.3 million tons, the U.S.S.R. with 1 million tons, and Canada with 720,000 tons accounted for 67 percent of the world total. As indicated in table 10 production of primary aluminum in the North American continent, compared with total world output has declined from 60 percent of the world output during 1954–58, to slightly less than 50 percent in 1963.

Statistical information on the consumption of aluminum in the United States by industries or by end products is incomplete. Total apparent consumption of aluminum, calculated from primary production and primary producers' stock changes, net imports of crude, semicrude and scrap, and recovery from scrap, is shown in table 11. These figures do not allow for stock changes at any consumption level, at secondary smelters, nor for metal going to government stocks.

During 1954–58 imports accounted for an average of 11 percent of the total supply of aluminum, and from 1959 to 1963 an average of about 10 percent of the total supply was imported. Canada, Norway, France, and Japan have been the chief sources of imported aluminum.

Prior to 1959 domestic exports of aluminum were quite small averaging only about 2 percent of the total supply during 1954–58. In 1959, about 6 percent of the total supply was exported, and in 1960, 13 percent was exported. The average for 1959–63 was 8 percent.

The tariff duties on several aluminum products, effective at the end of 1963, were as follows:

Item	Rate of duty Aug. 31, 1963	Statutory rate of duty
Unwrought (in coils)	2.5¢ per pound.	0.7¢ per pound.
Unwrought (other than aluminum silicon alloys).	1.25¢ per pound.	0.4¢ per pound.
Wrought (bars, plates, sheets, strip).	2.5¢ per pound.	0.7¢ per pound.

Source: Tariff schedules of the United States, effective Aug. 31, 1963.

TABLE 8.—*Sources of aluminum supply-crude and scrap*

[Thousand short tons]

Year	Primary production	Recovery from scrap [1]		Imports [2]	Total supply	Exports [3]
		Old	New			
1954–58 (average)	1, 584	69	255	237	2, 145	46
1959	1, 954	78	282	250	2, 564	150
1960	2, 014	63	267	159	2, 503	357
1961	1, 904	102	238	205	2, 449	202
1962	2, 118	128	333	317	2, 896	210
1963	2, 313	115	389	433	3, 250	229

[1] Aluminum content.
[2] Aluminum metal and alloys, crude, plus ingot equivalent, (wt × 0.9) of scrap.
[3] Aluminum ingot, slabs and crude, plus ingot equivalent (wt × 0.9) of scrap.

TABLE 9.—*World production of aluminum*

[Thousand short tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963
United States	1, 584	1, 954	2, 014	1, 904	2, 118	2, 313
U.S.S.R.[1]	500	690	745	990	1, 000	1, 060
Canada	596	594	762	663	690	719
France	160	191	263	308	325	329
Japan	73	110	147	169	189	247
Norway	97	161	182	189	227	242
Germany, West	155	167	186	190	196	230
Italy	69	83	92	92	90	101
Austria	61	73	75	75	82	84
Switzerland	33	38	44	47	55	67
India	8	19	20	20	39	61
Cameroon	[2] 22	47	48	52	58	58
Other communist countries [1]	129	221	260	333	341	352
Other free world countries	93	132	147	173	185	232
Total	3, 580	4, 480	4, 985	5, 205	5, 595	6, 095

[1] Estimated.
[2] 1957–58.

TABLE 10.—*World production of aluminum by continents*

[Percent]

Continent	1954–58 (average)	1959	1960	1961	1962	1963
North America	61. 2	56. 9	55. 7	49. 3	50. 2	49. 7
Europe	35. 2	36. 5	37. 4	43. 0	41. 1	40. 9
Asia	2. 9	4. 8	5. 3	5. 9	6. 3	7. 1
Africa	. 3	1. 0	1. 0	1. 0	1. 0	1. 0
Oceania	. 2	. 3	. 3	. 3	. 3	. 8
South America	. 2	. 5	. 3	. 5	1. 1	. 5
Total	100. 0	100. 0	100. 0	100. 0	100. 0	100. 0

TABLE 11.—*Apparent consumption of aluminum in the United States*

[Short tons]

Year	Primary sold or used by producers [1]	Imports (net) [2]	Recovery from old scrap [3]	Recovery from new scrap [3]	Total apparent consumption
1954–58 (average)	1, 562, 421	200, 606	68, 924	254, 911	2, 086, 862
1959	1, 988, 560	139, 828	78, 006	281, 921	2, 488, 315
1960	1, 866, 251	−180, 057	62, 703	266, 747	2, 015, 644
1961	1, 956, 167	24, 004	102, 137	238, 109	2, 320, 417
1962	2, 184, 876	117, 935	127, 756	332, 734	2, 763, 301
1963	2, 353, 626	174, 548	115, 164	389, 263	3, 032, 601

[1] Includes shipments to the Government: 1957, 324,311 tons; 1958, 323,128 tons; 1959, 73,235 tons; 1960, 37,002 tons; 1961, 52,138 tons; 1962, 41,544 tons; 1963, 24,293 tons.
[2] Crude and semicrude. Includes ingot equivalent of scrap imports and exports (weight multiplied by 0.9). Includes some shipments to Government stockpiles: Figures not available.
[3] Aluminum content.

STRATEGIC CONSIDERATIONS

Figure 1 illustrates the degree of self-sufficiency in the United States with respect to aluminum metal. Inasmuch as most of the imported aluminum comes from Canada and the domestic production capacity is dispersed (see table 3), the strategic position of the United States with respect to aluminum metal is good. However, as discussed in the Alumina and Bauxite chapter, domestic supplies of economically competitive bauxite are limited, and in 1963 imports accounted for 86 percent of the total new supply of bauxite. Consequently, both bauxite and aluminum have been acquired in various Government stockpiles. On June 30, 1964, Government inventories of aluminum totaled 1.9 million tons, of which 1.1 million was in the national (strategic) stockpile and 0.8 million was in Defense Product Act stocks. Stocks of aluminum oxide totaled 378,000 tons, of which 200,000 was in the national (strategic) stockpile and 178,000 was in the supplemental stockpile.

The primary aluminum industry is especially vulnerable to a loss of electrical power. If the power to a reduction cell is interrupted, it will freeze in a few hours and it takes 6 to 8 days to obtain metal from the cell after the power is restored. If power to a potline is lost, it may take several weeks to reach maximum production in the entire line.

GOVERNMENT PROGRAMS

The Government, through direct financing or incentives, has encouraged expansion of the aluminum industry from the mine through semifabricating facilities. Government programs have focused on promotion of a competitive industry and have resulted in the entry of new producers and assured that part of the

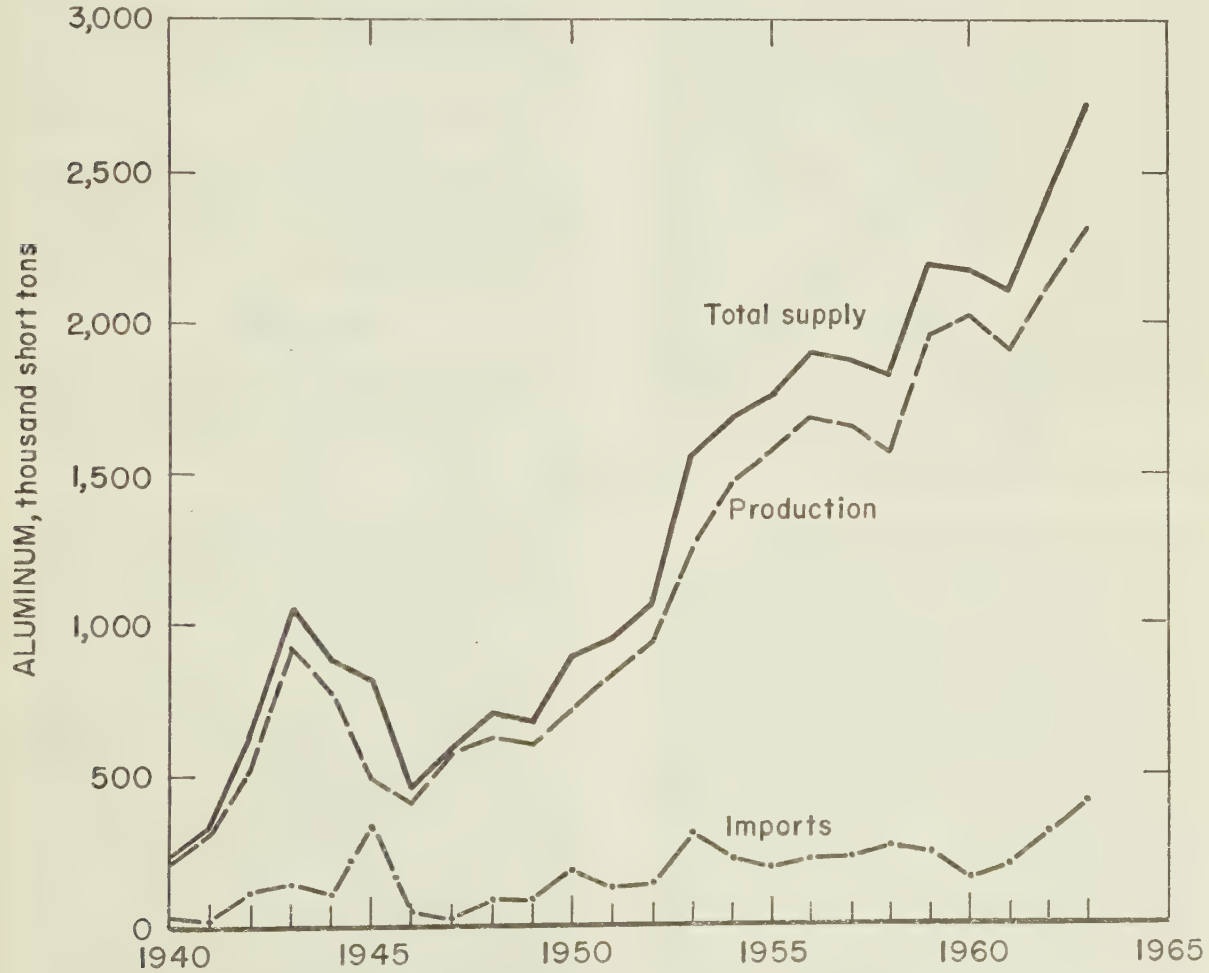

FIGURE 1.—New Supply of Primary Aluminum in the United States.

production from the new facilities would be made available to nonintegrated consumers of crude aluminum. Government policies relating to the development of power in agricultural areas have also had a profound effect on the formation and location of the industry.

Under the impetus of both World War II and the Korean War, domestic primary aluminum capacity expanded sharply. During these periods (1941–45 and 1951–52) aluminum came under the Controlled Materials Plan and the metal was distributed under a system of priorities.

After the war Government plants, which were not economically competitive, were sold and converted to nonaluminum uses. Those which could be operated competitively were sold to Alcoa, Reynolds, or Kaiser (then Permanente Metals Corp.). After disposal of the Governments plants, domestic primary aluminum capacity was 680,000 tons.

The pattern of the industry was unchanged from 1946 until the Korean War. From 1951 through 1954 inclusive, 613,000 tons of Government-aided capacity came into production. Expansion during this period differed from World War II expansion in that none of the facilities were owned by the Government and all were located near electric power sources, which would permit economic operation of the plants in peacetime. The Government issued accelerated tax amortization certificates and entered into market guarantee contracts with the companies in the early 1950's. Market guarantee contracts with Alcoa and Kaiser expired late in 1958, and the contract with Reynolds expired in 1959. The contract with Harvey Aluminum, Inc., expired in 1963.

Under these guarantees, the producers shipped 876,000 tons of aluminum to the Government between 1957 and 1963.

PRICES AND COSTS

The aluminum industry's price policy probably has been an important factor in the rapidly increasingly usage of the metal by many consuming industries. While prices of other major nonferrous metals increased between 100 to 150 percent from 1939 to 1959, the price of aluminum ingot increased only 34 percent during the same period. The average price of aluminum ingot in 1925 was 28.2 cents per pound and gradually decreased to the World War II price of 15.0 cents per pound. The first increase was in 1948, but the 1925 price was not approached until August 1957 when the postwar high of 28.1 cents per pound was reached. From 1957 until late 1963 the quoted price for aluminum ingot gradually declined to 22.5 cents per pound. In October 1963 the price was increased to 23 cents per pound.

Prices quoted at the end of 1963 for various grades of aluminum scrap clippings ranged from 11.5 to 12 cents per pound for 2075 (75S) to 15.5 to 16 cents per pound for 1100 (2S). Mixed aluminum clippings were quoted at 14 to 14.5 cents per pound. Old aluminum sheets and castings were quoted at 12 to 12.5 cents per pound, and aluminum borings and turnings were quoted at 12.5 to 13 cents per pound.

Effective September 27, 1963, quoted delivery prices for 10-ton lots of various grades of smelters' alloys ranged from 21 to 21.5 cents per pound for 380 (AXS–679) alloy containing 3 percent zinc to 29.25 to 29.75 cents per pound for 218 alloy grades. Steel deoxidizing grades ranged from 19.5 cents per pound for 85 percent aluminum (minimum) grade to 23.25 cents per pound for 95 percent aluminum grade.

One company reported the following mill costs (in cents per pound of pig) for 1953 (*23*):

Raw materials (includes alumina at cost including transportation and alloying materials)	4.71
Energy (for reduction only)	2.93
Manufacturing costs	6.43
Total	14.07

Transportation costs on shipments of pig, general administrative expense, and selling expense brought the total cost to 16.20 cents per pound of pig. The average price of pig in the United States in 1953 was 19.7 cents per pound.

RESEARCH

The high rate of growth in the aluminum industry has been maintained by aggressive marketing practices and a large and continuing research effort to develop new products and improve efficiency from the reduction cell. Industrial research covers the entire field of metal production, through the development of alloys and casting techniques, the study of protective and decorative finishes, and detailed investigations of end use applications of the metal. The producers develop technical data for their own use, as well as for the use of their customers.

Improvements in operation of the reduction cell that were under investigation, included the use of lithium fluoride in the electrolytic bath and new materials of construction for cathodes. Kaiser Aluminum & Chemical Corp. and British Aluminum Co. Ltd. developed a modified type of reduction cell which utilized refractory hard metal compounds instead of carbon as electrodes. Typical materials considered for this application were the carbides and diborides of titanium and zirconium. If the new cathode

materials and the improved electrolyte prove satisfactory, the total increase in production capacity per cell could be as high as 50 percent.

Aluminium Ltd. in Canada conducted pilot-plant studies of its process for producing aluminum from an impure metal made by direct reduction of bauxite. Aluminum trichloride was reacted with the impure metal at 1,000° to 1,200° C to form aluminum monochloride, which was subsequently cooled to about 700° C and decomposed to pure aluminum metal and to the trichloride, which in turn was recirculated. Based on the experience of operating its pilot plant, the company completed construction of a new installation at Arvida in 1963 and planned to determine capital and production costs which would be expected from large-scale operation of the process.

Another direct reduction process, developed by Péchiney of France, also was believed to be operating on a pilot-plant scale. In the French process, bauxite is partially reduced with carbon in an electric furnace, then it is further reduced with carbon to produce a mixture of aluminum and aluminum carbides. The aluminum was separated and the aluminum carbide recycled. Reynolds Metals Co. reportedly tested a direct reduction thermal process in a pilot plant of undisclosed size.

Many other methods of recovering aluminum have been proposed. Such processes include the treatment of alumina with aluminum sulfide and carbon at an elevated temperature; hydrogen reduction of alumina at above 100 atmospheres and above 400° C; reaction between alumina and aluminum carbide at 1,980° C; and electrolytic reduction of complex alumino-organic compounds such as $NaF.2Al(C_2H_5)_3$.

Direct smelting of aluminum-silicon alloys from clay has been investigated. High-purity clay is used to minimize contamination of the alloy by iron and titanium. An electric furnace with graphite electrodes has been used with a carbon reductant, which may be coke, charcoal, sawdust, hogged fuel, or mixtures of these materials. At operating temperatures pure aluminum would volatilize or react with oxides of carbon. This is prevented by the addition of silicon which alloys with the aluminum and promotes absorption of the aluminum vapors (*4*).

Methods for recovering commercial-grade aluminum from Al-Si alloys have been investigated. Experimental procedures have included leaching the alloy with a molten metal such as zinc in which the aluminum dissolves and the silicon and impurities are relatively insoluble. The zinc is then distilled from the dissolved aluminum. In the subhalide process a crude aluminum alloy is treated with $AlCl_3$ at approximately 1,000° C to produce AlCl. The reaction is reversed by lowering the temperature; pure aluminum condenses and the $AlCl_3$ vapors are recycled.

Bureau of Mines programs on aluminum have emphasized the development of processes to extract alumina from low-grade bauxite or non-bauxite materials, as discussed in the Alumina and Bauxite chapter. However, studies have been made on carbothermic reduction of domestic clays to purchase aluminum-silicon alloys, from which the aluminum could be recovered. The Bureau operated a laboratory-scale alumina reduction cell to study the fundamental physical chemistry of the electrolytic process, and the effects of changes in certain operating variables which might be interpreted in terms of plant-scale operation (*15*).

OUTLOOK

Projections of the annual rate of increase of aluminum consumption range from 6 to 10 perpent, or about 2 to 3 times the growth of the gross national product, compared with the average rate of 11 percent per year since 1900. Consumption in the United States, which was about 30 pounds per capita in 1963, is expected to grow at a slower rate than in the rest of the world, which on a per capita basis uses less than half as much aluminum as the United States.

Apparent consumption of primary aluminum, calculated from production, imports (metal and alloys, crude), exports (ingots, slabs, and crude), and changes in producers and Government stocks, provides a convenient measure of the demand for primary aluminum. The average annual growth in this measure of aluminum demand in the United States was slightly over 8 percent from 1946 to 1963. Assuming an increase of 8 percent per year, and using 1963 as the base year, apparent consumption of primary aluminum in the United States in 1968 will be 3.85 million tons, and by 1975 will reach 6.6 million tons.

The extent to which foreign trade might account for total supply of primary aluminum in a given year is not easily predicted owing to unrelated factors in the countries involved. In 1963, many domestic companies had or planned to have substantial financial interests in foreign reduction facilities, which suggests that imports will play an increasing role in the domestic market. In addition, economic trends indicate that new reduction facilities will tend to be built in areas with available low-cost power and high-grade bauxite instead of the major market

areas such as the United States. However, aluminum demand in emergent and moderately industrialized countries is expected to expand much faster than in the United States, and it is not likely that the share of imports of primary metal in the U.S. market will increase significantly.

From 1948 to 1963 imports of crude aluminum metal and alloys accounted for 11 to 24 percent of the apparent consumption of primary aluminum in the United States and averaged 14 percent per year. Assuming that imports will account for 15 percent of the projected apparent consumption, imports will be about 580,000 tons in 1968 and will reach nearly 1 million tons by 1975.

Prior to 1959 domestic exports of crude and semicrude aluminum metal were insignificant compared with the total apparent consumption of primary aluminum; however, in 1959 exports were 6 percent of the total, rose to 17 percent in 1960, and averaged about 7 percent from 1961 through 1963. Assuming that exports of primary metal will continue at about 7 percent of the projected consumption, the United States will export 270,000 tons in 1968 and 460,000 tons in 1975.

Neglecting changes in producer's inventories of primary aluminum domestic production should be about 3.4 million tons in 1968. Assuming no changes in industrial or Government stocks, domestic production of primary metal should be about 6.1 million tons in 1975. An average annual increase of 8 percent will be necessary to attain the projected output.

No plans for building new reduction plants in the United States were reported in 1963, but producers had scheduled increases in capacity of existing facilities to 2.8 million tons. Provided these expansions are completed an additional 600,000 tons of primary capacity will be needed by 1968, which might be attained through further expansion of facilities existing in 1963 and by construction of 3 or 4 new plants by 1968.

During and immediately after World War II aluminum recovered from scrap averaged about 40 percent of the apparent consumption of primary aluminum. However, from 1951 to 1963 total recovery of aluminum metal from scrap, estimated by the Bureau of Mines, has ranged between 20 and 30 percent of the apparent consumption of primary metal, the average being about 25 percent. Assuming that aluminum recovery from scrap will be 25 percent of projected consumption of primary metal, 960,000 tons of aluminum will be recovered from scrap in 1968, and by 1975 about 1.6 million tons will be recovered. It may be that the share of secondary aluminum in the over-all market will increase to more than 25 percent, owing to increasing supplies of old scrap as uses expand.

The construction and transportation industries should continue to provide the major outlets for aluminum metal through 1975; however, the relative use in these industries, which comprised 48 percent of the market in 1963, is likely to decline somewhat, because of rapidly expanding markets in other industries, especially in containers and packaging, and electrical conductors.

Free world production of primary aluminum is expected to continue to increase about 8.5 percent annually as it did in 1959–63. If this rate is maintained, 7 million tons of primary aluminum will be produced in the free world in 1968 and 12.5 million tons in 1975, compared with 4.7 million tons in 1963. The growth of aluminum production in the Communist countries probably will also increase at about 8 to 9 percent per year, reaching 2.1 million tons in 1968 and 3.7 million tons in 1975, compared with 1.5 million tons in 1963.

Intensive research accompanied by laboratory and pilot-plant studies will continue to search for new processes to recover aluminum and aluminum compounds from various aluminous ores. Economic direct reduction processes may be developed by 1968, but they are not likely to replace the Bayer-Hall facilities for many years because of the large investment in such facilities. Accordingly, the major short-term technologic changes in the industry will center upon improvements of the Hall cell operation. New reduction plants of less than 20,000-ton-per-year capacity may utilize direct reduction techniques.

PROBLEMS

Maintenance of an adequate aluminum supply requires assured ore supplies as well as continuation of research on improving processes for recovering the metal from various raw materials. The industry is faced with the problem of acquiring adequate quantities of low-cost electric power or decreasing the high energy consumption in producing aluminum.

Dusts and fumes in the effluent gases from the aluminum reduction cell represent a loss of alumina, carbon, and fluorides, and systems that collect and scrub the effluent gases represent a large capital investment.

Inasmuch as the production of aluminum is a semibatch process, the producers are faced with the high costs inherent in such an operation.

Refractories used in furnaces for melting scrap or alloying primary aluminum are attacked or penetrated by the molten metal. The recovery of aluminum from some types of scrap is quite low. Fines and dusts containing both metallic aluminum metal and aluminum oxide are discarded.

Some of the physical properties of aluminum, such as its poor strength characteristics at elevated temperatures, its softness in comparison to cast iron, lack of corrosion resistance at high temperatures or in contact with other metals, may be obstacles to the use of aluminum in special applications.

Facilities that have higher operating costs than modern plants or are poorly located with respect to markets are closed in time of surplus aluminum supplies. Closing a plant of this type results in the idling of a large capital investment and may cause some economic dislocation.

The high initial plant investment and the difficulty of obtaining an assured long-term alumina supply discourage potential aluminum producers. Small nonintegrated consumers of ingot or semifabricated aluminum, numbering the thousands, do not have assured supplies of metal.

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ANTHRACITE

By J. A. Vaughan [1]

LIKE other coals, anthracite was formed from vegetable matter deposited in bogs and swamps during the Carboniferous age, which was ended by a violent series of earth movements known as the Appalachian revolution. Under the tremendous pressure and heat created by this upheaval of the earth's crust, the carbonaceous material metamorphosed into anthracite—with the volatile components being driven off in varying degrees. As a result, anthracite is a low-volatile (2 to 8 percent on a dry basis), hard, compact coal that generally breaks with a conchoidal fracture. Difficult to ignite, anthracite is long-burning, with a clean, blue smokeless flame that makes it a desirable domestic fuel.

About 95 percent of the U.S. reserve of anthracite lies in 10 counties of northeastern Pennsylvania. Other anthracites occur as relatively small deposits in Arkansas, Colorado, New Mexico, Virginia, and Washington; however, because they are classified as semianthracites, their production is included in the chapter on Bituminous Coal and Lignite. The metaanthracite field in Rhode Island and southeastern Massachusetts, which has been mined sporadically in the past, has no present economic significance.

During its long history Pennsylvania anthracite has made important contributions to the economic and industrial development of the country, both as a fuel and as a source of carbon. Approximately 5.3 billion short tons has been mined and shipped to market, and the remaining reserve (estimated as adequate to supply projected demand for several centuries) still represents one of the country's most important mineral fuel resources because of its magnitude and easy accessibility to the densely populated, highly industrialized eastern seaboard. (See fig. 1).

Peak production of approximately 100 million tons was reached in 1917 and the highest employment, about 180,000 men, in 1914. However, owing to the inroads made into anthracite's traditional space-heating markets by competitive fuels, particularly fuel oil and natural gas, production had declined by 1963 to 18.3 million tons. Since the anthracite industry had provided the base of the regional economy for so many decades, the declines in production and employment caused many serious social and economic problems for the industry and the counties comprising the producing region.

As part of its work in the fields of mineral resource conservation and development, the Bureau of Mines, in cooperation with the producing industry and others, is actively pursuing a comprehensive research program designed to improve the technology of mining, preparing, and utilizing anthracite. Through such efforts, it is hoped that production costs can be lowered and new uses found—especially in industrial and metallurgical processes—that will make the industry less dependent upon the space-heating market. Other Bureau efforts are directed toward the conservation of reserves through a cooperative Federal-State mine-water control program, which provides for the installation of deep-well pumps and the construction of surface facilities to divert surface water away from active underground workings. As an adjunct to the mine-water control program, abandoned underground mine voids are being backfilled with incombustible material to prevent surface subsidence and its attendant hazards to the public health and safety.

BACKGROUND

Early records indicate that Pennsylvania anthracite was first used by gunsmiths about 1755. In 1769, it was burned successfully in a blacksmith's forge and, in 1808, in an open grate without forced draft by Judge Fell at Wilkes-Barre. These events caused no great stir, however, because firewood was abundant and cheap and the industrialization of the country was still in its infancy.

[1] Mineral specialist (coal).

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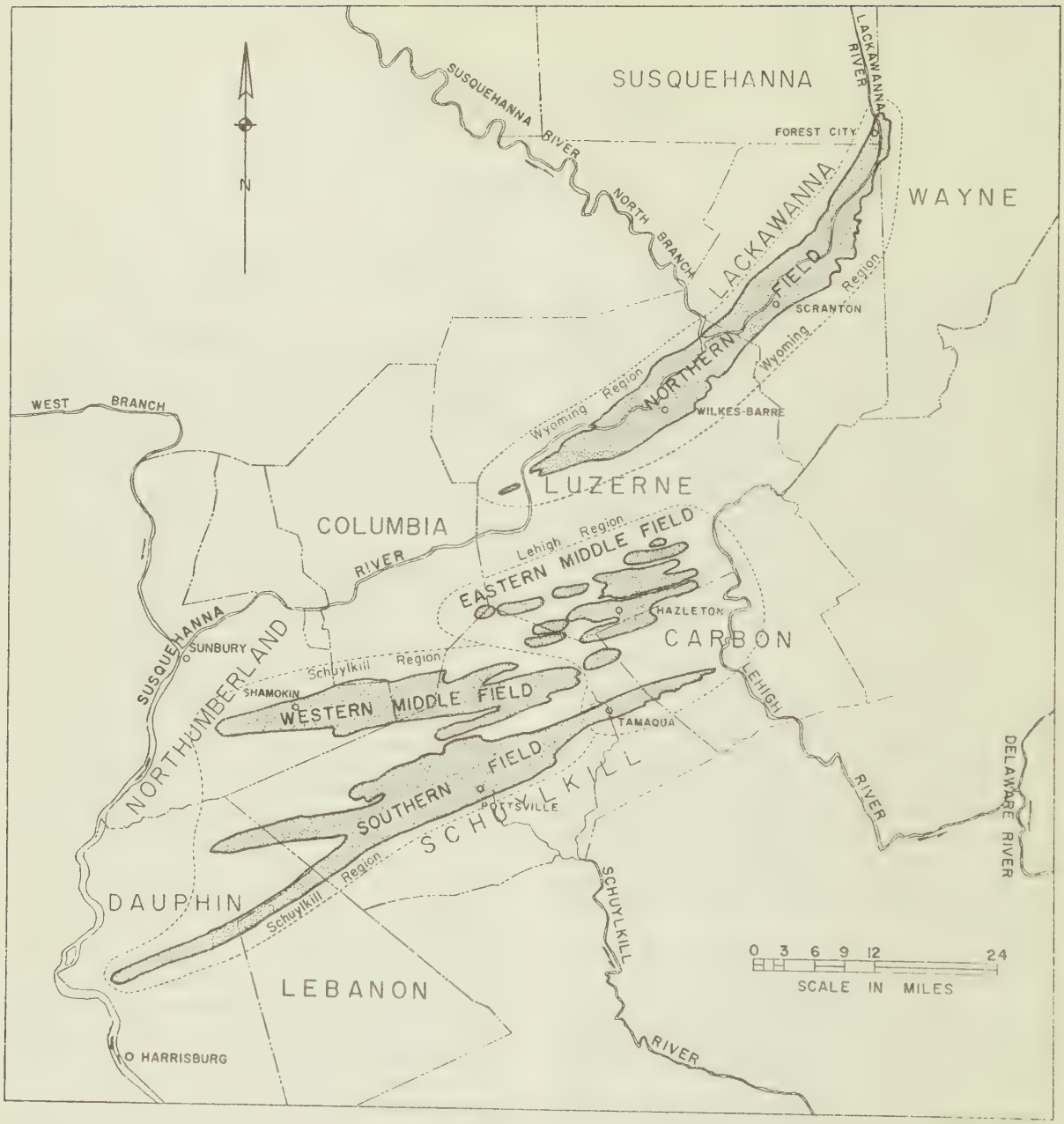

FIGURE 1.—Coalfields of the Anthracite Producing Region of Pennsylvania.

Soon after the beginning of the 19th century, charcoal and fuelwood became scarce and expensive as forests contiguous to the rapidly growing urban areas of the Middle Atlantic and Southern New England States became depleted. By 1817, a number of small anthracite mines had been opened, but it was not until 1829 that shipments were made from all the producing fields. As the highway system was crude and in some areas virtually nonexistent, the cost of transporting bulk commodities overland was prohibitive. Thus, the earliest shipments of anthracite were made by wooden "arks," or barges, which were floated down-river to market and later broken up and sold as lumber.

Seasonal variations in water flow and the dangers involved in transporting anthracite by this method, stimulated the search for cheaper and more reliable means of transporting bulky materials to distant markets. Thus, the first effort

to establish an inland canal system in the United States was engendered to stimulate demand for Pennsylvania anthracite from the Lackawanna, Lehigh, Schuylkill, and Wyoming Valleys.

A segment of the Schuylkill Canal, the first completed, was used in 1818, but it was not until 1825 that the canal was opened officially, linking Pottsville with the important Philadelphia market. Subsequently, other canals were completed that enabled anthracite to move into New York City and New England coastal cities.

The next important development in the transportation of anthracite was the creation of "feeder" lines from the mines to the canals. These lines were known as gravity "railways," with small loaded cars running downhill to the canals over wooden rails covered with strap iron. The empty cars were then pulled back to the mines by horses or mules. The first such line started operating in 1827 and connected mines to the Lehigh Canal at Mauch Chunk (now Jim Thorpe), a distance of 9 miles.

The anthracite industry also contributed another "first" to the industrial development of our country, the railroad. The famous "Stourbridge Lion" was the first steam locomotive used in this country, with the epochmaking round trip between Honesdale and the present site of Seeleyville being made on August 8, 1829. In a relatively short time thereafter all of the anthracite fields were laced by railroad trackage and the canals slowly fell into disuse.

The first statistical record of anthracite production is for 1807–20, during which 12,000 short tons was mined. With the development of first the canal system and then the railroads, anthracite production moved steadily upward until the record output of 100 million tons was reached in 1917. Peak employment, approximately 180,000 men, occurred in 1914. However, in the early 1920's heating oil began to make serious inroads into anthracite space-heating markets. By the 1930's natural gas also began to loom as a competitor, a threat that materialized fully with the spread of gas pipelines into the heavily populated cities of the Middle Atlantic and New England States after the close of World War II. By 1938, output had fallen to 46 million tons. With the advent of the war, however, anthracite production climbed rapidly, totaling 64 million tons in 1944. From this point anthracite production declined steadily under the vigorous competition of other fuels, except for a few years in which small gains were registered because of increased demand in export markets. Although higher than production in 1962, total production was only about 18.3 million tons in 1963.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

The 18.3 million tons of Pennsylvania anthracite produced in 1963 was the total output of 834 underground mines, 200 strip pits, 112 culm and silt banks, and 15 dredges. Run-of-mine coal from underground mines and strip pits and material from banks was cleaned and sized in 127 preparation plants (breakers and washeries). Dredge operators cleaned and sized their output as it was recovered from the streams draining the anthracite fields.

The operating structure of the anthracite industry is highly complex, ranging from the small two-man operation to large integrated units consisting of mines, pits, surface shops, and preparation plants employing several hundred. The large operating companies usually control a number of mines, strip pits, preparation plants, and in some instances, substantial quantities of recoverable coal in culm and silt banks. In 1963, the 15 largest producers accounted for about 65 percent of the total output. Many of the small operations are individual underground mines or strip pits which primarily produce run-of-mine coal for sale to preparation plants. Also, a number of the preparation plants have no mining facilities but purchase their entire input from independent producers of run-of-mine coal.

Although a few producing companies maintain their own sales organizations, the larger part of the tonnage shipped from preparation plants by rail is sold to consumers by wholesalers, dock operators, and exporters. Truck tonnages, on the other hand, are usually handled at the preparation plant and move to market as—(1) sales to consumers in the immediate vicinity of the mines (local sales); (2) sales to over-the-road truckers who dispose of the coal at retail; and (3), sales to retail dealers who dispatch their trucks to pick up loads at the plants.

The Pennsylvania anthracite beds lie in 10 counties of the northeastern part of the State: Carbon, Columbia, Dauphin, Lackawanna, Lebanon, Luzerne, Northumberland, Schuylkill, Susquehanna, and Wayne. (See fig. 1.) The Bernice Basin, lying a short distance west of the Northern field, contains a small deposit of semianthracite that is included with the Northern field for statistical purposes. The coal measures underlie a surface area of 484 square miles and are separated by geologic conditions into

four fields, the Northern (176 square miles), Eastern Middle (33 square miles), Western Middle (94 square miles), and Southern (181 square miles). Mining operations are conducted in each of the fields.

The anthracite-producing region is also divided by the coal trade into three regions: The Wyoming, which is coextensive with the Northern field; the Lehigh, composed of all the Eastern Middle field and that part of the Southern field lying east of Tamaqua; and the Schuylkill, which includes the entire Western Middle field and that portion of the Southern lying west of Tamaqua. Of the 1963 total, excluding dredge coal, 46 percent was produced in the Schuylkill region, 33 percent in the Wyoming, and 21 percent in the Lehigh. Among the fields, the Northern led with 33 percent of the 1963 total (again excluding dredge coal), followed by the Southern with 28 percent, the Western Middle with 24 percent, and the Eastern Middle field with 15 percent. Luzerne, Schuylkill, Northumberland, and Lackawanna Counties, the four largest producers in that order, accounted for 89 percent of the year's total output.

DEFINITION OF GRADES, SIZES, AND SPECIFICATIONS

Because of its characteristics, the most efficient combustion can be attained only with anthracite that has been properly cleaned and sized. Despite multimillion-dollar preparation plants capable of consistently producing a high-quality product, large quantities of poorly prepared coal were marketed during the depression years of the 1930's and World War II. The General Assembly of the Commonwealth of Pennsylvania, in an attempt to protect consumers against inferior coal, passed Act 168, approved May 31, 1947, to regulate the sale, resale, and shipment of anthracite. This act (known as the anthracite standards law) with amendments approved May 18, 1949, and September 26, 1951, not only required the issuance of a written statement as to the quality of the anthracite being shipped, and providing penalties for misrepresentations therein, but established the legal specifications for "standard" anthracite shown in table 1. Provisions of the act are administered by the Anthracite Committee, an agency of the Commonwealth.

TABLE 1.—*Standard anthracite specifications approved and adopted by the Anthracite Committee, effective July 28, 1947*

Size	Round test mesh (inches)	Percent					
		Oversize, maximum	Undersize		Maximum impurities [1]		
			Maximum	Minimum	Slate	Bone	Ash [2]
Broken	Through 4⅜				1½	2	11
	Over 3¼ to 3		15	7½			
Egg	Through 3¼ to 3	5			1½	2	11
	Over 2⅞		15	7½			
Stove	Through 2⅞	7½			2	3	11
	Over 1⅝		15	7½			
Chestnut	Through 1⅝	7½			3	4	11
	Over 13/16		15	7½			
Pea	Through 13/16	10			4	5	12
	Over 9/16		15	7½			
Buckwheat No. 1	Through 9/16	10					13
	Over 5/16		15	7½			
Buckwheat No. 2 (Rice)	Through 5/16	10					13
	Over 3/16		17	7½			
Buckwheat No. 3 (Barley)	Through 3/16	10					15
	Over 3/32		20	10			
Buckwheat No. 4	Through 3/32	20					15
	Over 3/64		30	10			
Buckwheat No. 5	Through 3/64	30	No limit				16

[1] When slate content in the sizes from broken to chestnut, inclusive, is less than above standards, bone content may be increased by 1½ times the decrease in the slate content under the allowable limits, but slate content specified above shall not be exceeded in any event. A tolerance of 1 percent is allowed on the maximum percentage of undersize and the maximum percentage of ash content. The maximum percentage of undersize is applicable only to anthracite as it is produced at the preparation plant. Slate is defined as any material that has less than 40 percent fixed carbon. Bone is defined as any material that has 40% or more, but less than 75 percent, fixed carbon.

[2] Ash determinations are on a dry basis.

An analysis of a typical chestnut-size Pennsylvania anthracite from the Lehigh region, with a heating value of 13,390 Btu per pound is as follows:

Proximate (percent)		Ultimate (percent)	
Volatile matter	3. 6	Ash	9. 3
Fixed carbon	87. 1	Sulfur	. 4
Ash	9. 3	Hydrogen	2. 1
		Carbon	85. 5
		Nitrogen	. 7
		Oxygen	2. 0

Note: Calculated on a dry basis.

TECHNOLOGY

Geology

The Pennsylvania anthracite beds occur in the Pottsville and post-Pottsville formations of the Pennsylvanian system of the Carboniferous age. The carboniferous age was ended by a violent series of movements of the earth's crust, known as the Appalachian revolution. During this period pressure developed from the southeast, causing the horizontal Carboniferous and other sedimentary formations to give way. Moving northwestward, the formations rose into mountain-forming folds, or peaks. Close to the pressure source, the folds were steep and, in some areas, overturned beyond the vertical. The continuity of the coal beds was frequently interrupted by slip-faults, or strata breaks, that displaced the bed-planes up to several hundred feet. As the distance from the pressure source increased, however, the folds became more gentle.

Under the pressures and heat generated by this vast crustal movement, the carbonaceous material in the measures metamorphosed into anthracite—with the volatile constituents being driven off in varying degrees. The clays and sands separating the beds were transformed into shales, hard sandstones, and conglomerates. In time, erosion, continuing through and subsequent to the Appalachian revolution, removed a large part of the folds and left only remnants of the original coalbeds. The anthracite measures contain from 12 to 26 minable beds, which are separated by 2 feet to 200 feet of shale, sandstones, or conglomerate. The coalbeds themselves range from a few inches to as much as 60 feet thick. Where the strata have been tightly folded, local areas have been found where a coalbed might be 100 feet thick.

Structurally the Pennsylvania anthracite fields are the remains of synclinoriums, or major downfolding of rock formations. Within the synclinoriums, minor folding formed synclinal troughs, or basins. In the northeastern part of the Northern field the coalbeds are relatively flat-lying in the center but pitch moderately to steeply toward the outcrops. In the southwestern part of the field the coal measures reach a depth of more than 2,000 feet, and have a complex system of minor folds and faults in the center with steep pitches toward the outcropline. The Eastern Middle field is composed of a number of separate, long, narrow basins in which the beds pitch steeply toward the center of each. The coal measures in the Western Middle field are characterized by steep pitches along the sides of the basins and a complex system of moderate folds and faults in the center. As the Southern field was subjected to perhaps more pressure than the others, the field is typified by pronounced folding and faulting. The coalbeds lie at extreme angles in relation to the surface, with some outcropping vertically or actually being overturned. In some places the coal has been so crushed as to run when it is mined.

Mining

The methods used in producing Pennsylvania anthracite from its various sources—underground mines, strip pits, culm banks, and streams—vary from the relatively simple suction devices employed by dredge operators to the extremely complicated underground mining systems required in extracting steeply pitching beds of thick coal.

In the earlier days of anthracite mining virtually all of the output was obtained at underground mines, since strip mining had to await the development of adequate excavating equipment. The burning equipment then in use resulted in vast quantities of pea and smaller sizes being dumped either onto culm banks or into the streams traversing the coal measures. Later, when the combustion equipment required to burn the small sizes become available, the culm banks and rivers became important sources of useable material—particularly because the initial mining cost had already been paid. Also, in recent years, the necessity of minimizing price increases occasioned by raising labor, materiel, and other costs has forced producers to close high-cost deep mines, concentrate mining at the most efficient operations, and resort to strip and bank coal for a larger percentage of their output.

As a result of the foregoing, underground mining has gradually assumed a secondary role in anthracite production. For example, in 1948 deep mines produced 65 percent of the annual output. However, as shown in table 2, produc-

tion at deep mines had dropped to 51 percent of the total in 1958 and only 37 percent in 1963. On the other hand, strip production moved from 32 percent of the total in 1958 to 41 percent in 1963, and culm-bank coal from 14 to 18 percent over the same period. Dredge production has averaged about 700,000 tons per year for 1956–65.

TABLE 2.—*Production of Pennsylvania anthracite, 1958 and 1963, by fields and source*

[Thousand short tons unless otherwise specified]

Field	From underground mines	From strip pits	From culm banks	From river dredging	Total	Percent
1958:						
Eastern Middle	264	942	532	----------	1,738	8
Western Middle	2,567	2,371	1,045	69	6,052	29
Southern	2,579	1,737	771	610	5,697	27
Northern	5,289	1,828	555	12	7,684	36
Total	10,699	6,878	2,903	691	21,171	100
Percent	51	32	14	3	100	----------
1963:						
Eastern Middle	70	1,410	1,177	----------	2,657	14
Western Middle	1,383	2,083	804	36	4,306	24
Southern	2,276	1,876	706	656	5,514	30
Northern	2,985	2,099	706	----------	5,790	32
Total	6,714	7,468	3,393	692	18,267	100
Percent	37	41	18	4	100	----------

Underground Mining

The conventional systems of mining in the Pennsylvania anthracite region are—Chamber and pillar; breast and pillar; and, to a small extent, slant chute. However, in some flat, deep areas with heavy cover, part, or all, of the pillars are recovered later in "robbing" and third-mining operations.

The chamber-and-pillar method is generally used in flat and slightly to moderately pitching areas, regardless of the thickness of the coalbed. With this method, chambers are driven 24 to 30 feet wide and up to 300 feet long—leaving coal pillars 26 to 36 feet wide between the mined-out chambers to provide support for the overlying strata. This method particularly applies to the Northern field; however, where such support is not required, the pillars are subsequently recovered.

The breast-and-pillar system is used in steeply pitching areas. With this method, "breasts" (called "rooms" in flat areas) about 24 feet wide are driven up the pitch, usually on 50-foot centers, with supporting pillars being left between them. As the coal face is blasted off, some of the loose coal is allowed to accumulate in the "box," which is formed by the manways constructed on both sides of the breast as the coal face is advanced. The box, which is kept filled, thus not only provides roof support but a working platform for the miners. The loose coal is drawn from the boxes after the breast is completed and before "robbing," or pillar recovery, begins. Some operators use a 34-foot center and do not attempt pillar recovery because a major part of the pillar generally "squeezes out" when the box coal is drawn.

The latter system is one of two relatively recent advances in pitch-mining techniques that have increased safety and the percentage of recovery. By omitting the pillar-robbing phase of the pitch-mining cycle the most hazardous part of the work has been largely eliminated. The other advance has been achieved by the introduction of long-hole pitch mining, a form of longwall. In using this method, the only work performed above the "monkey heading," or return airway, is driving two narrow breasts (about 150 feet long) to the upper level and 12-foot long stubs, on 50-foot centers, above each chute. Holes about 2 inches in diameter are then drilled 100 to 120 feet up the pitch in the solid coal. The holes are then loaded and fired consecutively away from the near, shorter breast, thus providing an opening for the loose coal. The stubs are then driven to facilitate blasting and loading operations.

Aside from some experimental work, underground mechanization in the Pennsylvania anthracite region is limited by the geologic characteristics of the fields to mechanical loading

and haulage. The most common equipment used for these purposes are hand-loaded face conveyors, scraper loaders, and mobile loaders. Of the total loaded mechanically underground in 1963, 78 percent was in the Northern field (96 percent of the total produced at deep mines in this field), where the coalbeds are relatively flatter than in the others.

Strip Mining

Anthracite stripping techniques and equipment have been so improved that the depth and extent of an operation is limited almost entirely by the ratio between the overburden and the thickness of the coal bed.

Anthracite strip pits vary in size and extent from shallow excavations along a steeply pitching outcrop, which may be worked by a single small dragline, a bulldozer, and a few men to the removal of a complete synclinal trough, or basin, hundreds of feet deep and extending over several hundred acres. (See figs. 2 and 3.) The larger strippings require intricate engineering planning and working procedures, as well as the use of many large shovels, draglines, and auxiliary equipment. Excavators of over 30-cubic-yard capacity are in use, and one operator plans to install a 62-cubic-yard dragline in the near future. Auxiliary equipment used consists of drills capable of drilling 9-inch blastholes in hard rock at a rate in excess of 1 foot per minute, 70-ton-capacity off-the-road trucks, and large bulldozers and graders.

FIGURE 2.—View of Greenwood Mining Company's Deep Anthracite Strip Pit Near Tamaqua, Pa.

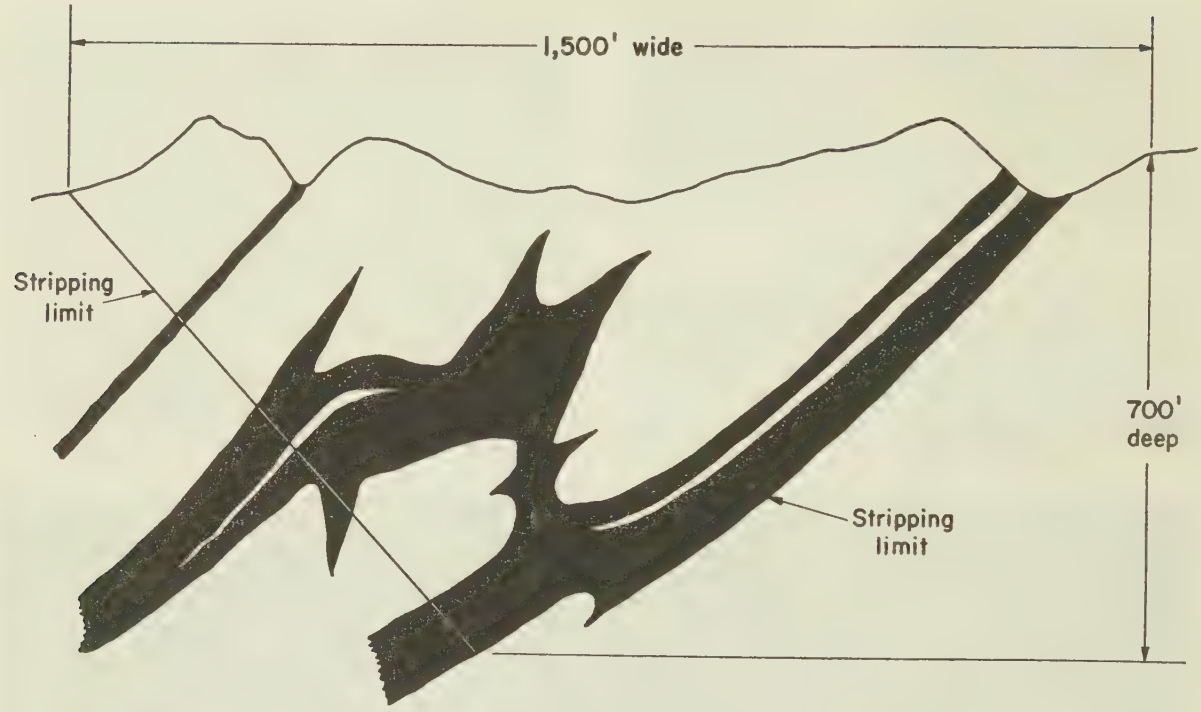

FIGURE 3.—Typical Cross Section of Coalbeds in Greenwood Stripping (fig. 2).

Culm and Silt Banks

Because of the low cost of recovery, the old culm and silt banks laid down in the early days of anthracite mining have been for several decades an important source of small-sized anthracite. Formerly a waste product of the preparation plants, the culm material is simply loaded into trucks by shovel and transported to preparation plants where it is cleaned and sized into a marketable product. The public utility industry particularly consumes large quantities of silt, ultrafine carbonaceous material that was deposited in separate banks as waste, that is not reprocessed in a preparation plant.

River or Dredge Coal

Because much of the preparation-plant wastes in the early days of anthracite mining was discharged directly into streams, or eroded into them from culm and silt banks, the beds of the Susquehanna, Schuylkill, and Lehigh Rivers, as well as many of their tributaries, eventually became covered by substantial quantities of small-sized anthracite. Since the immersion in water caused virtually no deterioration in the quality of the coal, these deposits also became valuable when combustion equipment capable of handling the finer sizes became available. The recovery of coal from the river beds started in the late 1800's with simple suction devices and dewatering screens mounted on barges, a procedure that is still followed except for the use of clamshell buckets by some operators.

Preparation

The raw feed to anthracite preparation plants, whether from deep mines, strip pits, or banks, contains varying amounts of impurities, such as slate, "boney coal" (a slaty or argillaceous material), "tramp" iron, wood, and so forth, and ranges in size from fines to massive pieces. The primary function of the preparation plant, therefore, is to break the large pieces, remove the impurities, and separate the coal into standard sizes.

The first anthracite preparation plant, locally termed "breakers," was constructed in the Southern field in 1844 and was capable of sizing 200 tons per day. During the ensuing decades, numerous cleaning, sizing, and dewatering techniques were developed—culminating in plants having capacities of cleaned, sized coal of 2,000 tons per hour, a high degree of automation, and low manpower requirements.

Virtually all coal-cleaning methods now in use are based primarily upon the difference in specific gravity of coal and its impurities. Jigs, which clean coal by rapid pulsations of water, were once widely used in the anthracite industry

but now play only a minor role in anthracite preparation. Cones, first introduced in 1921, are still in general use for cleaning larger sizes. Coal separation is achieved in the cone (which obtains its name from its overall shape) by maintaining a sand and water mixture, which is agitated by a revolving paddle in the center, at a gravity slightly higher than the coal—thus permitting the coal to float off and the refuse to sink. However, in another type of cone, similar results are achieved by setting a coal-and-water mixture into a swirling motion by water nozzles placed in the sides of the cone. Heavy-media equipment utilizing mixtures of magnetite and water has also gained wide acceptance for cleaning the pea and larger sizes.

Hydro-separators, or classifiers, using the principle of slow water currents and hindered settling, are used widely for cleaning the smaller sizes. Concentrating tables are utilized in a number of plants for cleaning the smaller coals. Also used for this purpose are launder screens, which since their introduction have been adapted to fine-coal cleaning by several operators.

For fine and ultrafine sizes (buckwheat No. 2 through 200-mesh), the anthracite industry first began to use flotation equipment about 1940, and there are a number of plants with this type of equipment. The most recent addition to the line of fine-coal cleaning equipment is the cyclone, which operates by the use of centrifugal force in conjunction with either water or a magnetite slurry.

USES

As with many other mineral commodities, definitive end-use data are relatively limited for Pennsylvania anthracite; however, uses fall into the following two broad categories: (1) As an energy fuel and (2) as a source of industrial carbon.

Anthracite is produced in a wide range of sizes (see table 1), each of which might be used for different purposes; however, some generalizations may be drawn as to size-use relationships. For instance, the sizes used for space-heating in homes may range downward from egg to buckwheat No. 2, with pea and larger being considered the hand-fired sizes. The automatic, or stoker-fired, sizes include some pea coal and buckwheat Nos. 1 and 2 (rice), while relatively large quantities of buckwheat No. 3 (barley) are used in automatic equipment for heating commercial establishments such as hotels, apartments, and office buildings. The barley not used for commercial heating and buckwheat No. 4 and smaller sizes are generally classified as industrial-purpose coals. Exceptions to these broad classifications are egg coal, most of which is used in the United States for gasmaking, and small quantities of buckwheat Nos. 1 and 2 used for industrial purposes.

Since the inception of mining over 150 years ago the space-heating market has been the largest outlet for anthracite, and until the advent of oil- and gas-burning equiment, Pennsylvania anthracite was the primary domestic fuel in the Middle Atlantic States, New England, and the eastern Provinces of Canada.

Public utilities are the second largest consumer of Pennsylvania anthracite. However, the trend in this market has been downward—dropping from about 3.4 million tons in 1957 to approximately 2.2 million tons in 1963. See table 4. While the sources of public-utility coal are not completely known, the larger part is undoubtedly high-ash fine material recovered at low cost from old culm and silt banks and from creeks and rivers.

The iron and steel industry is the third largest consumer of anthracite, using about 1.9 million tons in 1963 for the manufacture of coke, sintering iron-ore fines, pelletizing beneficiated low-grade domestic iron ores, lining pots and molds, heating, as an industrial carbon, and as a substitute for coke in foundries. In 1960, the last year for which data are available, class I railroads consumed about one-quarter million tons of anthracite, virtually all of which was thought to have been used for heating purposes.

Anthracite is used in manufacturing briquets, in bakeries, for burning cement and lime, in brick and ceramic kilns, curing tobacco, hay, and other agricultural products, in greenhouses and hatcheries, and in other applications where clean, steady heat is essential.

As a carbon, anthracite is used for a wide variety of purposes. Small quantities are used in telephones, as water and chemical filters and purifiers, in manufacturing battery cases, electrodes and other electrical or electronic equipment, carbides, and for making carburetted water gas. Anthracite ash is not only an excellent soil conditioner but is used widely in manufacturing lightweight building blocks. As a semiprecious stone, anthracite is used by local artisans to create jewelry and objects of art.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Except for some mine rock and anthracite ash that have been used in manufacturing lightweight building aggregates and mine refuse used as fill, there are no important byproducts or coproducts of present anthracite mining.

ALTERNATE MATERIALS

The present pattern of fuel consumption in the United States has been formed by such diverse factors as the availability of a particular fuel in a given locality, the industrialist's desire to obtain fuel or power at the lowest cost, homeowners' concepts of convenience, and demand for the unique physical or chemical characteristics possessed by an individual fuel. Natural gas, fuel oil, coke, briquets, wood, and other fuels all compete with anthracite for use in the space-heating field. The most common expression for changes in fuels use are "conversion" and "replacement," which indicate, first, the adaptation of existing burning equipment to the use of an alternate fuel and, second, a change of the heating plant to one designed to burn another fuel.

Because of its physical characteristics, anthracite has advantages as a space-heating fuel not possessed by any other fuel. The cost of burning the smaller space-heating sizes is lower in many areas, on a Btu basis, than either natural gas or fuel oil. Efficient, automatic combustion equipment is available for both domestic and commercial heating purposes. Nevertheless, many consumers consider natural gas and fuel oil more convenient because the use of anthracite requires storage space and ash removal. Also, manufacturers of anthracite heating equipment have not succeeded in producing plants that can be installed as cheaply as gas and oil burners. Thus, anthracite has not only lost a major part of its space-heating market through conversions but has not captured an appreciable share of the market represented by new construction.

In industrial applications, several hundred thousand tons of anthracite are used annually in the manufacture of metallurgical coke, either displacing bituminous coal or to impart certain characteristics to the coke. The amount used annually as a substitute for coke breeze or bituminous coal in sintering and pelletizing iron-ore fines also totals several hundred thousand tons. Small quantities are charged directly to furnaces and foundry cupolas in place of metallurgical coke, while moderate amounts are used as industrial carbon for the manufacture of electrodes, carbides, and carbon shapes.

RESERVES

In estimating remaining recoverable reserves of Pennsylvania anthracite the Federal Geological Survey assumed past mining losses were 50 percent. Accordingly, the Survey placed total remaining reserves at 12,355 million tons as of January 1, 1960, and recoverable reserves at 6,178 million tons. However, in 1921, the weighted average recovery during first mining was estimated at 40.9 percent and for second mining, 24.5 percent. The residual, 34.6 percent, represented coal lost in underground mining. An additional 4.3 percent was estimated to have been lost in preparing the coal for market. Thus, in 1921, the recovery rate from underground operations was established at 61.1 percent. However, since 1921, improvements in both mining and preparation practices have reduced mining losses. Any estimate of present minable anthracite reserves would be unrealistic unless the following factors were given proper consideration: (1) The relatively rapid growth of strip mining; (2) coal recovered by dredges and from culm and silt banks, which was undoubtedly included as losses in earlier calculations; (3) the quantity of reserves that have been irretrievably lost by mine flooding; (4) the quantity of pillar coal that may be recovered or that must be left intact to support mine openings, the surface, or to safeguard active workings from adjoining, flooded mines; (5) coal lying under municipalities which have restricted mining within their jurisdictions; (6) unmined areas providing support for highways, bridges, streams, and so forth; (7) the economic feasibility of mining thin beds; and (8) the tonnage of anthracite destroyed by mine fires.

CONSERVATION PRACTICES

Improvements in mining and preparation practices since 1921 probably have reduced this estimated total loss and helped to conserve coal. The long-hole method, as an adjunct to the breast-and-pillar mining system, and improved methods of pillar recovery are examples of techniques which have increased the percentage of recovery. Similarly, modern preparation equipment, such as the heavy-media systems, recover a larger percentage of the raw-coal feed than the older types of equipment.

Important from the conservation standpoint also is the intensive development of stripping equipment and methods, since virtually 100 percent of the coalbed is recovered. Another important conservation development has been the recovery and use of anthracite from culm and silt banks and rivers. The coal recovered from these sources is the small-sized material that was formerly discarded by the preparation plants as unmarketable.

Mine water is a serious problem in the anthracite region that not only imposes heavy pumping costs upon some producers but threatens to inundate large reserves of coal. An overall approach to this problem has been provided by the mine-water control program established in 1955. The Federal and State Governments

have each contributed $8.5 million to purchase and install pumping plants and facilities to improve surface drainage. Coal-producing companies cooperate by paying operating and maintenance costs after the facilities are installed. The Federal Government is represented by the Department of the Interior, through the Bureau of Mines.

The mine-water control program has been a factor in preventing the flooding and loss of coal reserves. Through its surface-drainage improvements, the program also aids in the conservation of water resources by preventing surface water from seeping into the mines and forming acid solutions that ultimately would be pumped to the surface and contaminate the streams.

SOURCES OF STATISTICAL INFORMATION

All known producers of Pennsylvania anthracite are canvassed annually by the Bureau of Mines for data on production by sizes, f.o.b. mine values, source of coal—both by type of mining and by county, field, and region—and the number and types of mechanical equipment used in mining operations. These data, plus the information on employment collected in conjunction with the survey on coal-mining injuries, are published in the Pennsylvania Anthracite chapter of the Bureau of Mines Minerals Yearbook, volume II.

Coal-year data (Apr. 1–Mar. 31) are collected by the Bureau on shipments of Pennsylvania anthracite, by sizes, to more than 100 key cities in 20 States and Canadian Provinces. As producing companies frequently are not aware of the final destination of some shipments, wholesalers, sales agents, dock operators, and exporting firms are also canvassed. The resulting data are released annually in a Mineral Industry Survey, Distribution of Pennsylvania Anthracite, and include, in addition to the city data, statistics on exports and methods of transportation.

Monthly data on stocks and retail dealer deliveries of anthracite are obtained by the Bureau through a sample survey of a number of representative dealers. Estimates are prepared from these sample data for publication as supplements to the Weekly Anthracite Report and in the Minerals Yearbook.

In preparing weekly and monthly estimates of production, the statistical summary of monthly developments, and the Pennsylvania Anthracite chapter of the Minerals Yearbook, data are assembled from numerous sources. For instance, statistics on exports are supplied by the Bureau of the Census; on lake movement of anthracite by the Ore and Coal Exchange, Cleveland, Ohio; consumption by electric utilities, by the Federal Power Commission, and carloading data by the Association of American Railroads.

PRODUCTION, CONSUMPTION, AND TRADE

The first record of anthracite production in Pennsylvania was for 1807–20, during which 12,000 tons were shipped. Thereafter, production increased steadily until the record of almost 100 million tons was set in 1917. The production record since 1917 is outlined in table 3.

TABLE 3.—*Salient anthracite statistics*

[Thousand short tons unless otherwise specified]

Year	Production	Average value per short ton	Quantity loaded mechanically underground	Exports [1]	Imports [1]	Apparent consumption	Average number of employees	Average tons per man per day	Average hourly earnings [2]
1917	99,612	$2.85	[3]	6,007	13	94,100	154,174	2.27	[3]
1938	46,099	3.92	10,152	1,909	363	45,200	96,417	2.79	[3]
1944	63,701	5.57	14,975	4,186	12	59,400	77,591	2.79	$1.18
1954–58 (average)	26,140	8.47	6,587	3,572	2	22,900	33,280	4.14	2.48
1959	20,649	8.35	4,701	1,788	3	18,800	23,294	5.12	[4] 2.75
1960	18,817	7.82	4,044	1,440	1	17,600	19,051	5.60	2.75
1961	17,446	8.04	3,378	[5] 1,435	1	15,900	15,792	5.63	[6] 2.73
1962	16,894	7.94	3,065	[5] 1,802	8	14,300	14,010	5.92	[3]
1963	18,267	8.40	3,666	[5] 3,353	[7] 5	14,200	13,498	6.27	[3]

[1] U.S. Department of Commerce.
[2] U.S. Department of Labor.
[3] Data not available.
[4] 11-month average.
[5] Does not include shipments to West Germany for use at U.S. military installations.
[6] Discontinued with August; 8-month average.
[7] January–August data only; beginning with September these data are included with bituminous coal.

Anthracite consumption data shown in table 4 reveal the declining trend in the major use categories.

Oversea exports, primarily to Western Europe, have fluctuated widely in the past in response to wartime and postwar rehabilitation efforts, variations in ocean freight rates, costs of indigenous production, competition from Russian and other anthracites, and imports of petroleum.

Although the United States imported substantial tonnages of anthracite during strike periods and the depression years of the 1930's, the volume dropped sharply during World War II. By 1954, imports had declined to 6,000 tons and have not exceeded 10,000 tons since.

TABLE 4.—*Retail-dealer deliveries and consumption of Pennsylvania anthracite in the United States, by selected consumer categories*

[Thousand short tons]

Year	Retail dealer deliveries	Used as colliery fuel	Used by railroads	Used for generating electricity	Used in briquets	Used at cement plants	Used in the iron and steel industry—		
							For coke making	For sinter and pellets	For other uses
1959	7,562	129	292	2,629	43	159	369	780	683
1960	6,775	102	248	2,751	31	152	370	754	720
1961	5,070	45	(1)	2,509	28	153	320	588	685
1962	4,767	152	(1)	2,297	(2)	188	420	560	609
1963	4,055	161	(1)	2,155	(2)	184	451	766	670

[1] Data not available.
[2] Concealed to avoid disclosure of individual company data.

Sources: Reports by retail dealers, excluding local sales. Association of American Railroads; Federal Power Commission; and American Iron and Steel Institute.

TABLE 5.—*Anthracite exported from the United States*

[Short tons]

Country	1962	1963	Country	1962	1963
North America:			Asia:		
Canada	892,488	794,585	India	7,965	3,269
Mexico	5,325	7,319	Israel	9,277	10,867
Other countries	505	428	Japan		3,714
Total	898,318	802,332	South Vietnam	5,605	14,583
South America:			Other countries	221	552
Argentina	5,119		Total	23,068	32,985
Brazil	10,370	5,336	Africa		792
Venezuela	201	8,094	Oceania:		
Other countries	525	1,814	Australia	805	2,433
Total	16,215	15,244	Other countries		63
Europe:			Total	805	2,496
Belgium-Luxembourg	205,008	539,726	Grand total [1]	1,801,724	3,353,192
France	140,703	723,964			
Germany (West)[1]	244,011	52,163			
Italy	140,413	259,946			
Netherlands	133,183	829,118			
Spain		93,791			
Other countries		635			
Total [1]	863,318	2,499,343			

[1] Does not include exports to West Germany for use at U.S. military installations.

The U.S.S.R. has led the world for many years in the production of anthracite, with the United States running a distant second. Both of these countries are large exporters. In 1963, according to the Bureau of the Census, 3,353,000 short tons of Pennsylvania anthracite was exported, a gain of 86 percent over that of 1962, the total for which represented a gain of 26 percent over that of 1961. These figures do not fully reflect the total oversea movement of anthracite, however, because the Bureau of the Census does not include in its data coal shipped abroad for the use of U.S. Armed Forces. Based on figures furnished to the Bureau of Mines by the Association of American Railroads, 860,800 short tons was dumped at tidewater piers for shipment to West Germany in 1963 and 948,847 tons in 1962. By subtracting the Census data from these figures, it would appear that approximately 700,000 tons moved to our Armed Forces in West Germany in 1962 and about 800,000 tons in 1963.

Thus, in 1963, more than 4.2 million tons (or almost 1 ton out of every 4 produced) was exported. Although no size data were available, trade sources indicated the major portion of the 1963 export volume consisted of the larger sizes, thus helping the industry to withstand further losses in space-heating markets of the United States and Canada.

TABLE 6.—*World production of anthracite,[1] in principal countries*

[Thousand short tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963
Belgium	8,154	7,059	6,488	6,085	6,345	6,598
China [2]	6,440	22,000	24,800	22,000	22,000	22,000
France	12,655	13,785	13,683	12,849	12,942	[2] 10,260
Germany, West	12,947	13,902	13,257	13,803	14,351	14,969
Japan	1,619	1,781	1,987	2,088	2,065	1,982
Korea:						
North	[2] 2,340	6,101	7,471	[2] 8,300	[2] 9,900	[2] 10,700
Republic of	2,012	4,559	5,897	6,486	8,206	9,764
Netherlands [2]	4,375	4,400	4,400	4,400	4,400	4,300
South Africa, Republic of	453	777	709	1,429	1,224	1,270
Spain	2,680	2,888	2,771	2,863	2,913	3,094
U.S.S.R.	73,098	87,423	85,995	85,405	[2] 87,000	[2] 88,000
United Kingdom	4,693	4,039	4,026	3,973	4,371	4,658
United States, Pennsylvania	26,139	20,649	18,817	17,446	16,894	18,267
Vietnam, North	1,310	2,427	2,860	3,118	3,823	[2] 4,400
Other countries [3]	1,768	1,856	1,643	1,724	1,626	1,733
World total (estimate) [1]	160,700	193,600	194,800	192,000	198,100	202,000

[1] Data do not add to totals shown due to rounding where estimated figures are included in the detail.
[2] Estimate.
[3] Partly estimated.

NOTE.—An undetermined amount of semianthracite is included in the figures for some countries.

STRATEGIC CONSIDERATIONS

The anthracite fields of northeastern Pennsylvania are closer than any other mineral fuel to the major markets along the Atlantic north of Maryland. Hence, to the extent of its availability, anthracite is in a favorable position to replace other solid fuels which may become scarce in these areas during periods of emergency. However, despite an increase in production of about 25 percent between 1940 to 1944, supplies of anthracite were insufficient to meet expanded demand during World War II, and the Federal Government had to institute a strict allocation program to insure equitable distribution of the available coal. Although the anthracite industry can temporarily raise output above the 1963 level by working a fuller week and stepping up production at culm and silt banks, there is great doubt that it would be able to match its performance during World War II because of the rapid decline of underground mining and the scarcity of economically recoverable stripping sites.

PRICES AND COSTS

As anthracite is primarily a space-heating fuel, producing companies and their sales representatives customarily offer discounts on f.o.b. mine prices about April 1 each year to encourage retail dealers and consumers to purchase coal during the summer months. In 1963, the discounts averaged about $1.75 per short ton on egg, stove, and chestnut; pea, $0.50 to $0.70; buckwheat No. 1, $0.25 to $0.75; buckwheat No. 2 (rice), $0.25 to $0.50; and buckwheat No. 3 (barley), $0.40 to $0.50. In past years the spring discounts had been increased at stated intervals and in such increments as to establish the winter price schedule by the beginning of the heating season. However, in 1963, the spring prices remained in effect only a few weeks as a strong demand developed during the early summer months in the United States and Europe as an aftermath to the cold winter of 1962–63.

According to data published in the December 21, 1963, issue of Saward's Journal, wholesale prices being quoted, f.o.b. mine, were as follows: Egg, stove, and chestnut, $14.50 to $15.50 per short ton, or $0.75 to $1.00 higher than on an equivalent date in 1962; pea, $11.50 to $12.50, up $1.00 per ton; buckwheat No. 1, $10.50 to $11.00, up $0.50 to $1.25. Prices quoted on buckwheat No. 2 (rice) were virtually the same as for No. 1 ($10.50 to $10.75) and were also higher by approximately the same amount. No. 3 (barley), showing a slight weakness in demand, was quoted at $8.25 to $8.50, compared with $8.15 to $8.75 in 1962.

Retail, or delivered, prices of anthracite differ widely from the wholesale prices quoted in trade journals since they include margins of wholesalers or sales agents, rail or truck transportation costs, transshipment charges, costs of unloading and storage, local sales taxes, size-degradation losses, and retail dealer margins. The retail markup also varies markedly because of differences in yard-labor costs, the larger capital required to conduct business in large cities as compared with small towns, and other economic factors.

The differences that exist in retail prices of anthracite are illustrated by the monthly reports on fuel costs released by the Bureau of Labor Statistics. According to this source, in December 1963, stove and/or chestnut was sold at an average price of $33.50 per ton in Boston, $30.09 in New York City, $29.00 in Washington, D.C., $26.20 in Philadephia, and $24.37 in Baltimore. Buckwheat No. 1, a large portion of which is used in automatic equipment, retailed at $27.56 in Boston, $24.24 in New York City, $22.95 in Philadelphia, $21.84 in Washington, D.C., and $21.26 in Baltimore.

There are no reliable data available on costs of producing Pennsylvania anthracite, either in terms of cost per ton or by type of mining.

EMPLOYMENT, WAGES, AND PRODUCTIVITY

With the long-term decline in production, employment has declined steadily in the Pennsylvania anthracite mining industry. The average number of men working daily in 1963 totaled 13,498, or 49 percent less than were employed in 1958. Since total production declined only about 14 percent over the same period, it is apparent that the industry not only closed many underground mines with low productivity rates and concentrated underground mining at the most efficient sites but, at the same time, switched to strip pits and culm banks for a relatively larger percentage of their output. As a result of these efforts, output per man-day reached a record high in each year of 1958–63, with the 6.27 tons per man-day achieved in 1963 representing a gain of about 44 percent from the 1958 figure of 4.36 tons per day.

The Bureau of Labor Statistics, U.S. Department of Labor, terminated the monthly series of data on earnings in the Pennsylvania anthracite industry with the release for August 1961. On the basis of the 8 months reported, average hourly earnings in 1961 were $2.73 and weekly wages, $96.03. However, both of these figures are now probably higher as a result of the new wage agreement signed September 1, 1964, by major producers and the United Mine Workers of America. The package agreement included direct wage increases and such fringe benefits as three paid holidays, a $25 increase in vacation pay, and a revision of payments for lunch periods. The requirement that producers pay 70 cents into the union's health and welfare fund for each ton of cleaned coal produced was not changed.

TAXES

A corollary effect of the decline in anthracite production has been evident for some years in the field of taxation. Several companies with large coal reserves have claimed that local taxes, particularly upon coal lands the owners do not expect to exploit in the immediate future, placed a heavy burden on current operations. As a result of the claims lower assessments have been granted on coal lands, in some instances, that have benefited the operating companies; however, these reductions in the taxable real-estate base have forced some municipalities to either decrease expenditures or look elsewhere for revenue. In other cases, coal lands have been forfeited to local governments, which have obtained some income by leasing acreage to small operators.

As with bituminous coal, anthracite producers, when computing income for Federal income tax purposes, are allowed a 10-percent depletion allowance to compensate them for that portion of their reserves used in current production. The allowance is calculated at 10 percent of gross income from the coal property, but not to exceed 50 percent of the net income from such property.

TRANSPORTATION

Although Pennsylvania anthracite is shipped to virtually all sections of the continental United States and to many foreign countries, its principal markets are in the Middle Atlantic and New England States areas. These States usually provide outlets for approximately four-fifths of the annual production; however, because of a sharp increase in exports, the percentage taken by these areas dropped abruptly for the 1963–64 coal year (Apr. 1, 1963–Mar. 31, 1964). Of the 15.7 million tons reported shipped during that year, 67.4 percent moved to destinations in the New England and Middle Atlantic States combined, and about 7.1 percent to all other States. Exports totaled 25.5 percent (about 1 ton of every 4 shipped), with 21.3 percent moving to overseas destinations and 4.2 percent to Canada. (See fig. 4).

As shown in table 7, Pennsylvania is the anthracite industry's largest market—taking 41.6 percent of 1963–64 coal-year shipments—followed by New York with 14.7 percent and New

Jersey with 7.9 percent. In Europe, West Germany imported about 908,000 tons of Pennsylvania anthracite during the 1963–64 coal year (including coal shipped to U.S. Armed Forces in that country), followed in descending order by France with 828,000 tons, the Netherlands with 696,000 tons, Belgium and Luxembourg with 467,000 tons, Italy with 288,000 tons, and other European countries, 91,000 tons.

Truck shipments reported to the Bureau of Mines for the 1963–64 coal year totaled only 41.6 percent of total shipments as compared with 47.3 percent in the previous year. This decline was attributable in part to an actual decrease in tonnage, but the major reason was the sharp increase in overseas exports, all of which originates as rail shipments at the mines. Neverthless truck transportation of anthracite has grown rapidly in recent years. During the 1948–49 coal year 15.7 percent was shipped to market by truck compared with 50.5 percent in 1961–62. Several factors account for this development: (1) The relative stability of the market in the producing region, (2) increased rail freight rates, (3) larger truck capacities, (4) improved highways, (5) shorter turnaround time between mine and consumer, and (6) greater flexibility in retail dealer operations.

Rail rates on anthracite are seldom based on mileage. Therefore, it is generally found that the per-ton-mile rate tends to decrease in proportion to the length of haul. However, because operating costs of trucks remain relatively constant, the per-ton-mile cost factor limits anthracite trucking to areas within a radius of roughly 200 miles of the producing fields. Thus, present north-south economic trucking limits are represented by southern Connecticut and northern Virginia. The preponderant part of the Pennsylvania truck tonnage is delivered east of Harrisburg, with the northern sections

TABLE 7.—*Shipments of Pennsylvania anthracite by rail and truck, Apr. 1, 1963, to Mar. 31, 1964*

Destination	By rail		By truck		Total	Percent of total
	Short tons	Percent of total rail	Short tons	Percent of total truck	Short tons	
United States:						
New England:						
Connecticut	56,398	0.6	11,080	0.2	67,478	0.4
Maine	53,699	.6			53,699	.4
Massachusetts	257,243	2.8	4,237	.1	261,480	1.7
New Hampshire	35,289	.4	274	[1]	35,563	.2
Rhode Island	17,393	.2	227	[1]	17,620	.1
Vermont	57,794	.6	10,428	.1	68,222	.4
Total	477,816	5.2	26,246	.4	504,062	3.2
Middle Atlantic:						
New Jersey	739,882	8.0	496,468	7.6	1,236,350	7.9
New York	1,550,163	16.9	754,593	11.6	2,304,756	14.7
Pennsylvania	1,410,552	15.4	[2] 5,125,853	78.5	6,536,405	41.6
Total	3,700,597	40.3	6,376,914	97.7	10,077,511	64.2
South Atlantic:						
Delaware	13,317	.2	37,341	.6	50,658	.3
District of Columbia	21,833	.2	6,809	.1	28,642	.2
Maryland	275,869	3.0	77,790	1.2	353,659	2.2
Virginia	13,107	.1	718	[1]	13,825	.1
Total	324,126	3.5	122,658	1.9	446,784	2.8
Lake States:						
Illinois	71,628	.8			71,628	.5
Michigan	98,176	1.1			98,176	.6
Minnesota	9,958	.1			9,958	.1
Ohio	184,110	2.0			184,110	1.2
Wisconsin	38,519	.4			38,519	.2
Total	402,391	4.4			402,391	2.6
All other States	274,280	3.0	55	[1]	274,335	1.7
Total United States	5,179,210	56.4	6,525,873	100.0	11,705,083	74.5
Canada:						
Ontario	422,900	4.6			422,900	2.7
Quebec	223,582	2.4			223,582	1.4
Other Provinces	13,494	.2			13,494	.1
Total	659,976	7.2			659,976	4.2
Other countries	3,340,154	36.4			3,340,154	21.3
Grand total	9,179,340	100.0	6,525,873	100.0	15,705,213	100.0

[1] Less than 0.05 percent. [2] Includes local sales.

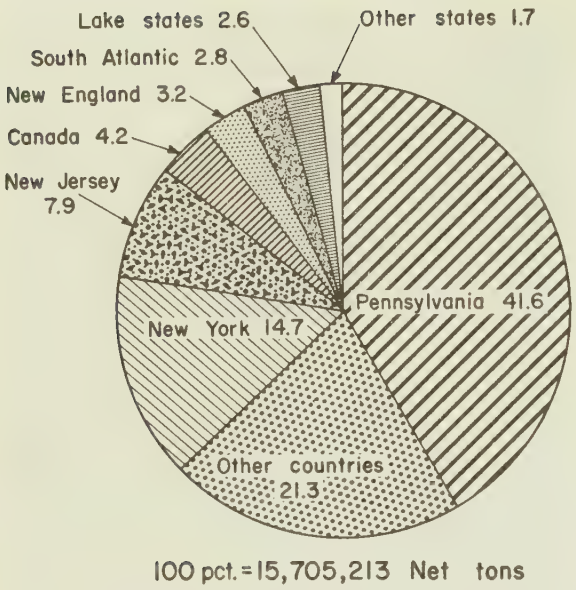

FIGURE 4.—Distribution of Pennsylvania Anthracite for the 1963–64 Coal Year, by Destination, in Percent of Total.

NOTE.—"Lake States" includes Illinois, Michigan, Minnesota, Ohio, and Wisconsin. "South Atlantic" includes Delaware, District of Columbia, Maryland, and Virginia.

of New Jersey and Delaware taking large tonnages. In New York, most of the trucked coal goes to New York City and counties in the southeastern part of the State while, in Maryland, Baltimore and the Eastern Shore are the major truck markets.

Except for occasional lake shipments to Canada, exported anthracite moves all-rail, whether to Canada or to the ports of Baltimore and Philadelphia for dumping into ocean-going vessels. Some other rail shipments are transshipped to final destinations via lake and tidewater. However, the coastal tidewater movement is virtually limited to the New York City-New Jersey area since shipments to New England, which once totaled several million tons per year, have practically ceased. The Lake trade in anthracite also has declined drastically in the past few decades, with loadings at Lake Erie and Lake Ontario docks totaling only 216,000 tons in 1963, compared with 1,322,000 tons in 1948.

GOVERNMENT PROGRAMS

The conservation of Pennsylvania anthracite reserves and the effects of mining operations upon the public health and safety are of continuing concern to both the Federal Government and the Commonwealth of Pennsylvania. In cases concerning mine water, mine fires, and surface subsidences, the Federal Government and the Commonwealth jointly provide technical and financial assistance to local municipalities and producing companies that are unable to cope with the problems involved.

To assist in maintaining an industry that would be economically capable of expanding output to fully meet defense requirements and to bolster the general economy of the producing region, the Federal Government has fostered a comprehensive research program designed to improve extraction, preparation, and utilization techniques. Research also has been conducted to develop new, or expand present, uses of anthracite—particularly in industrial and metallurgical processes. United States Armed Forces in West Germany began to purchase Pennsylvania anthracite as a replacement for German coke in the latter part of 1961. These purchases, which are designed to benefit the anthracite industry and the country's balance of payments, are expected to total about 1.1 million short tons in fiscal year 1964–65.

RESEARCH

Major anthracite research efforts have been directed primarily at reducing mining costs and creating new, or expanding old, uses. The attainment of these goals, however, has necessitated the conduct of investigations into many related fields such as the chemical and physical properties of anthracite, mining methods and equipment, the possible development of new products from anthracite, improved loading and haulage equipment, preparation techniques, and market studies.

Virtually all research in recent years has been under the sponsorship of the Commonwealth of Pennsylvania or the Federal Government. Most of the State's efforts have been coordinated by the Coal Research Board of the Commonwealth, and have been limited to special projects conducted by the Pennsylvania State University on the nature and distribution of the mineral matter content of anthracite, the effect of thermal shock on anthracite decrepitation, use of anthracite in making metallurgical coke, grindability tests, froth flotation of anthracite silts, and tests of anthracite at high pressures and temperatures. The State's efforts in the marketing field have been restricted to studies of the market-potential of Western European countries.

Since the establishment of the Anthracite Research Center at Schuylkill Haven, Pa., the Bureau of Mines has pursued a comprehensive and diversified research program on Pennsylvania anthracite. In the field of mining, much re-

search has been conducted in cooperation with producing companies. Among many projects undertaken have been the following: The development, or adaptation, of high-productivity mining machinery to moderate- and steeply-pitching beds; development of new roof-control methods to achieve a larger coal recovery and increased safety for the mineworkers; the development of a mechanized longwall mining system; the adaptation of continuous mining machines and augers to underground mining; improved loading and haulage techniques; yielding roof-support systems; hydraulic hoisting; and the hydraulic mining of anthracite at water volumes up to 300 gallons per minute and pressures up to 5,000 pounds per square inch, gage. (See figure 5.)

Conservation research conducted by the Bureau is concerned directly with investigations of the mine-water problem—including studies of the properties and characteristics of anthracite mine-water, and measures to control, or extinguish, mine and culm-bank fires. Other major, allied research efforts of the Bureau in the field of conservation are concerned with protecting anthracite reserves and the public health and safety. Conducted jointly by the Federal Government and the Commonwealth, projects in this field consist of constructing surface drainage improvements to prevent water from seeping into underground workings, where it may become acidic and ultimately contribute to stream pollution; installing deep-well pumps in abandoned mines to prevent flooding of reserves and protect workers in adjoining active mines; and, health and safety projects in which mixtures of water and incombustible material have been flushed into abandoned mineworkings to prevent, or alleviate, dangerous and costly surface subsidences. A project also was underway in 1964 to preserve on microfilm mine-maps of the anthracite producing region.

At the Anthracite Research Center, research on the utilization of anthracite has been directed primarily toward the development of large-tonnage markets. Studies of the decrepitation of anthracite under thermal shock were followed by tests of calcined (heat treated) anthracite in foundry cupolas. These tests were followed, in turn, by the successful formulation of anthracite metallurgical briquets which, after being calcined, demonstrated some properties equal or superior to metallurgical coke when tested in the Bureau's experimental blast furnace at Bruceton, Pa. Tests were also conducted at Bruceton on injecting buckwheat No. 5 and a boiler-grind anthracite into the furnace. Research conducted in cooperation with the Bethlehem Steel Co. on the permeability of blast-furnace stock columns was completed during 1964.

In attempts to discover some characteristics of anthracite that could lead to new uses, fundamental research conducted by the Bureau has included studies of mineral-matter distribution, chemical constitutents, the electrical resistivity of solid specimens, determinations of the density of selected samples of differing volatile content, surface-area measurements, and upon the effect of gamma radiation on anthracite, and on anthracite in the presence of other materials. Research into the chemical structure of anthracite was concentrated on oxidizing anthracite with nitric acid and identifying characteristics of the products obtained. Small amounts of anthracite were converted into methane in preliminary runs at 800° F and 300 to 800 pounds per square inch, gage in the miniscale hydrogasification plant constructed at the Research Center. Prior to these tests, anthracite was successfully gasified in commercial-scale Lurgi equipment.

In the field of preparation research, the Bureau has appraised various types of equipment to reduce anthracite to ultrafine particles (1 micron, or less); the production of a product containing 1 percent, or less, ash; and, the mechanical separation of anthracite-water slurries. Other efforts have included investigations of methods and equipment to obtain maximum yields of buckwheat Nos. 1 and 2 sizes when crushing chestnut coal; froth flotation; heavy-media separation; launder screens; grindability; and, washability characteristics of Pennsylvania anthracites.

Marketing research conducted by the Bureau is concerned with the production, distribution, and uses of anthracite, as well as with studies of particular markets, and the economic factors that affect fuel consumption.

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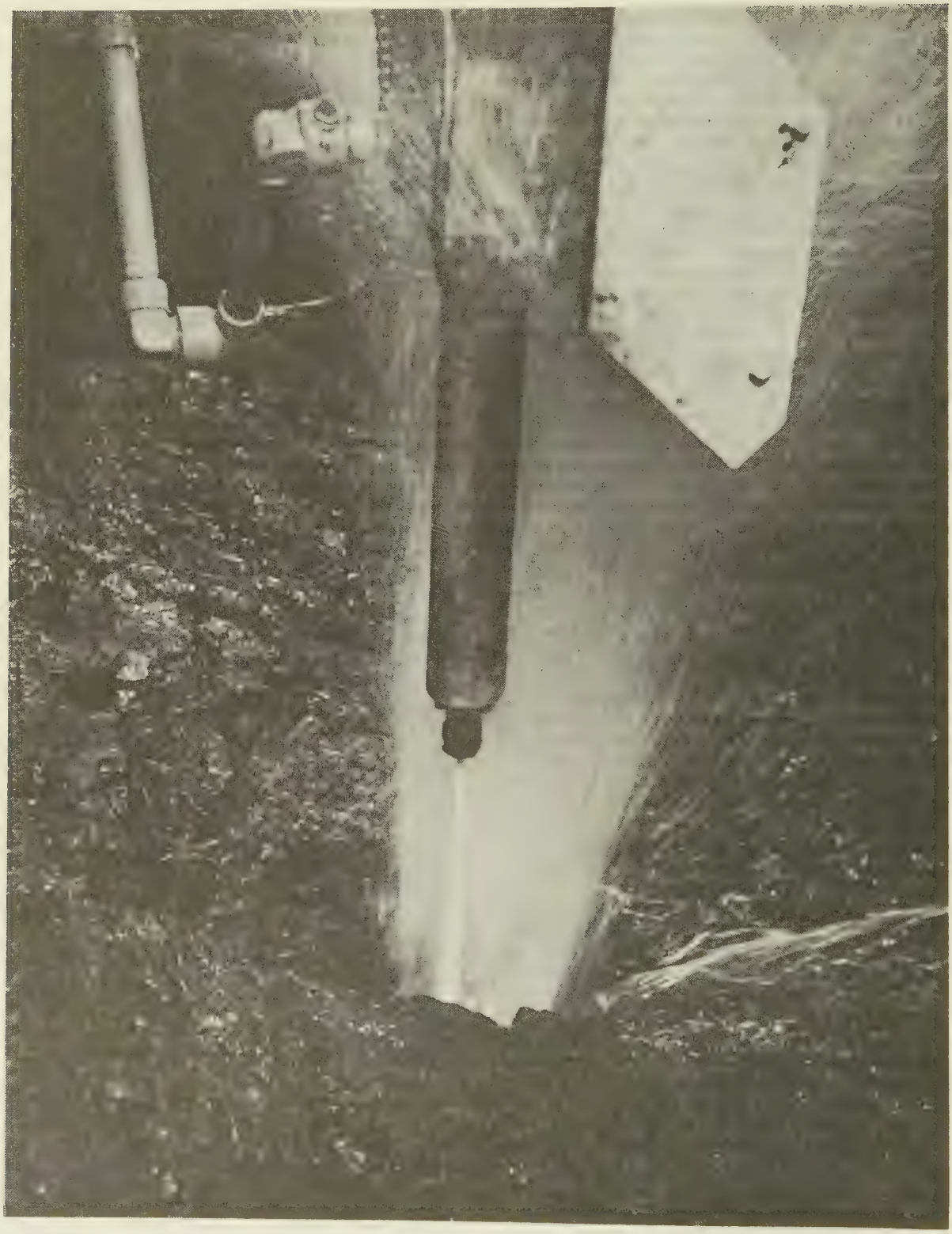

FIGURE 5.—Hydraulic Jet Cutting Anthracite Coal Face.

OUTLOOK

Few of the components of gross national product are satisfactory for forecasting the outlook for Pennsylvania anthracite. Since anthracite is used primarily as a space-heating fuel, it might appear that such criteria as anticipated growths in population and homebuilding are valid for projecting future demand. However, neither of these reflects the individual homeowner's concept of convenience or the reluctance of speculative builders to install coal-fired equipment in homes that are sold in competition with those equipped with less expensive oil- or gas-fired heating systems. Thus, the majority of new-home buyers actually have no choice of the fuel they will use and property owners who are faced with the necessity of replacing or converting their plants are discouraged from using coal by the difference in costs of the equipment. The anthracite industry, therefore, has had little success in capturing an appreciable part of the new-home or conversion markets. As a result, consumption of the space-heating sizes in the United States has decreased at an average annual rate of about 8 percent over the last 10 years, and is expected to continue to decline in the face of continued competition from petroleum, natural gas, and electric heating.

Natural gas reached Ontario and Quebec late in 1958, and shortly thereafter exports of the large space-heating sizes of Pennsylvania anthracite began to decline. Although the decrease in exports to Canada between 1958 and 1963 was at a greater rate than in space-heating markets of the United States, the future rate of decline in exports of space-heating sizes to Canada is expected to approximate that of the United States because of similar competitive conditions in the fuel markets of the two countries. Overseas exports of the large sizes appears to be fairly bright over a short term. In 1961, exports to Europe totaled slightly over 400,000 tons but reached 2.5 million tons in 1963, excluding 861,000 tons shipped to West Germany for use by United States Armed Forces. Of the 1963 total, about 60 percent consisted of pea and larger sizes. The Armed Forces in Europe may be expected to consume about 1 million tons per year for some time. Commercial shipments of the large sizes to Europe will probably vary widely from year to year—depending upon weather conditions, availability of indigenous supplies, competition from Soviet and other anthracites, and the rapidity with which petroleum and natural gas penetrate European space-heating markets. However, trade sources indicate that, despite these uncertainties, Europe will require between 1 to 2 million tons of American anthracite annually for the next few years, thus helping the industry to absorb the anticipated losses in United States and Canadian markets.

Although total demand for Pennsylvania anthracite is expected to decline, the immediate outlook for the smaller sizes (buckwheat No. 1 and smaller) appears to be brighter than that for the larger coals. The prospects for buckwheat Nos. 1, 2 (Rice), and 3 (Barley) have been enhanced by sales of automatic anthracite-burning equipment in the commercial field (apartments, hospitals, and schools), and the decline in the consumption of these sizes will probably be below that of the larger sizes. Consumption of the smaller sizes (No. 4 and smaller) by public utilities has decreased at an annual rate of approximately 4 percent during the past 5 years. As this market is based largely upon low-cost coal obtained from river dredges and old culm and silt banks, it, too, will continue to decline with depletion of these sources. This loss, however, is expected to be offset to some extent at least by a firm, and possibly increased demand, for the fine sizes for sintering and pelletizing iron ores, as an industrial carbon, and for other miscellaneous metallurgical uses.

No new large-tonnage markets for anthracite have been developed by research in recent years; however, investigations have been made, or are in progress, on the production of high Btu gas from anthracite; the substitution of calcined anthracite briquets for metallurgical coke in blast furnaces and foundry cupolas; production of low-ash coal for nonfuel purposes, and the production of chemicals by treating anthracite with selected reactants.

World reserves of anthracite are adequate to meet future demand although some areas, such as Western Europe, may have to rely more heavily upon imports to satisfy their requirements. In the United States, reserves are considered adequate to supply any foreseeable demand despite the factors mentioned in the Reserves section, which will adversely affect the quantity of coal that can be recovered economically.

PROBLEMS

The Pennsylvania anthracite mining industry is faced with physical and technologic problems that combine to keep underground mining costs at a high level. The difficulties of mining steeply pitching beds of hard coal not only contribute directly to higher costs but also limit the use of mechanical mining and loading equipment. This, in turn, has prevented an appreciable gain in underground output per man-day. Consequently, labor still represents a large part of total mining costs and will undoubtedly continue to do so until such techniques as long-hole mining, a modification of the longwall mining method, can be more fully adapted to steeply pitched seams.

In anthracite strip mining, costs are also generally higher than for bituminous coal because the steeply pitched seams and rolling surface topography of the region complicate the problems of hard-rock overburden disposal and pit drainage. Also, efficiency of the excavating equipment is adversely affected by restrictions of working areas as pit depths increase. This latter factor is assuming greater importance since stripping sites with shallow cover are almost exhausted, and operators are being forced to use larger equipment to work deeper coal to maintain an economically favorable coal-to-overburden ratio.

Pumping expense and mine-water control measures are important cost items in many areas. With the decline in production, numerous mines have been closed and their pumps stopped. As a result, abandoned mines have become flooded and are adding to the pumping load of adjoining active mines, thus further increasing underground mining costs. Although the Federal-State mine-water control program has proved highly successful in preventing surface water from seeping into underground workings and in maintaining certain underground pools at safe levels, mine-water control and pumping costs may become so excessive, in some districts, as to cause the closure of additional operations.

Pillar failure, generally caused by concentrated mining in beds overlying each other stratigraphically, and mine squeezes caused by the shifting weight of the rock strata overlying the coal bed, has resulted in a continuing, serious problem of surface subsidence in several heavily populated areas of the anthracite region. While the Federal and State Governments have made, and are making, a joint effort to prevent or alleviate damages resulting from caving and to preserve public health and safety, the number of seams that have been mined and the length of time that anthracite mining has been conducted indicate that the danger of possible future surface subsidences will require a long-term effort by the anthracite industry and the various governmental entities involved, particularly in the Northern field.

Mine fires are also a vexing problem in the anthracite region. In addition to destroying valuable reserves, the noxious fumes thrown off by these fires pose a threat to public health. Not only are they difficult and costly to extinguish, but underground fires create problems so serious that it is frequently necessary to close active mines. Fires in old culm banks are also of concern because of their possible adverse effects on public health and safety and the destruction of scenic values.

Problems connected with preparation practices are largely concerned with a diminution of losses and quality control. Modern coal-cleaning equipment and techniques have been installed at many preparation plants, with the result that losses have been decreased. However, greater emphasis must be given to a better separation of coal from its impurities and closer control over size consist if anthracite is to compete successfully in export markets where coal size, ash content, and volatile matter are critical factors. Notwithstanding the fact that United States and Canadian markets are accustomed to an anthracite containing more ash than is ordinarily used in Western Europe, competitive conditions in North American markets make it imperative for the industry to continue to supply a high-quality product at the lowest possible price to foster a satisfactory retail dealer-consumer relationship and to retain present consumers.

The larger space-heating sizes traditionally have furnished the bulk of the anthracite industry's revenue, with some of the smaller sizes being sold below actual production cost. The continued, substantial losses to competitive fuels in the space-heating field have led to occasional imbalances in the supply of the smaller sizes. A large part of the small coal marketed for industrial purposes is low-cost dredge, or "river," coal and material recovered from culm and silt banks, but these sources are being depleted rapidly. Ultimately, a greater percentage of the total demand for these sizes must be met from underground and stripping operations. Obviously, there is an upper limit on the prices that can be obtained for the small

sizes because they compete in the various industrial markets with other carbonaceous materials. Therefore, the overriding problem of the anthracite industry is to find new, profitable outlets for the pea and larger sizes to supply the demand for the full range of sizes produced.

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ANTIMONY

By Donald E. Moulds [1]

WORLD mine production of antimony was estimated at 64,000 tons in 1963 of which the free world contributed 56 percent and the Sino-Soviet bloc the remaining 44 percent. The United States requires approximately 41 percent of the world's new supply to supplement antimonial alloys regenerated each year from scrap. Other principal consumers are the industrial countries of Western Europe, Japan, and the U.S.S.R.

There is no significant domestic resource base. The domestic supply of antimony is obtained from imported ores, crude antimony, metal and oxide (44 percent), domestic mine production (2 percent), and scrap reclamation (54 percent). Domestic smelters produce primary metal and oxide from imported antimony ores and, also, as a byproduct antimonial lead from domestic and imported lead ores.

Antimony is essential as a metal for the production of antimonial lead for storage batteries plates, bearing-metal alloys, type-metal alloys and other alloys requiring its hardening, strengthening, and solidification-expansion characteristics. The oxide and sulfide enter a wide range of industrial applications such as enamels, paints, plastics, rubber, and glass manufacturing. Military uses of antimony are in ammunition primers, tracer bullets, shrapnel alloys, smoke generators, flame retardants, paints, and signal pyrotechnics.

Factors inherent in the geographical and mineralogical occurrence of antimony and those associated with demand have caused wide variances in the supply-demand balance. Because it is the world's largest consumer of antimony and presently lacks economic domestic ore supply, the United States must maintain the new supply required to support an expanding industrial use and to provide for national security.

BACKGROUND

Antimony is one of the oldest metals in continuous use by man. A vase cast in metallic antimony found among the ancient artifacts of the lower Euphrates valley discloses the fact that about 4000 B.C. the art of reducing the metal from the natural sulfide was known and practiced. Women of Biblical times used antimony as a cosmetic for eyebrow painting and recognized its medicinal qualities. Literature of medieval Europe in the 15th century alludes to liquation, precipitation, and "starring" of regulus, the refined antimony metal. Antimony was then in use in alloys for printer's type, mirrors, and bells. Precipitation of metal from the sulfide by iron is described by Ercker in the 17th century, and in the 18th century, roast-reduction procedures came into use. The early 1830's were marked by the reverberatory furnace; 1844 by the French volatilization process and 1896, by the first appearance on the market of electrolytic antimony.

Prior to the 20th century the chemical and metallurgical qualities of antimony found relatively small use. Annual consumption as measured by production was on the order of 7,500 tons. After the turn of the century consumption increased rapidly as the world industrial pace quickened and the low-cost, abundant supply of Chinese ore became available.

The wartime importance of antimony was first experienced in World War I when requirements for ammunition and antimonial-lead resulted in a shortage only partially alleviated by new production from U.S. mines and Bolivia. The postwar drop in demand caused a major antimony price depression and closure of mines unable to compete with low-cost Chinese antimony. Expansion of the auto-

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mobile industry and use of storage batteries stimulated consumption in the 1930's and in turn escalated secondary recovery of antimony. The Laredo, Tex., smelter placed in operation in 1930 expanded Mexican output, and the world's largest antimony producer, the Gravelotte mine in the Republic of South Africa, initiated production in 1935.

The Japanese invasion of China in 1937 abruptly cut off this source, but expanded output from Mexico and Bolivia maintained supply for the world rearmament program and the initial action of World War II. The escalated demand of the war years again reactivated mines in the United States and expanded production of foreign mines. Bolivia was the leading supplier followed closely by Mexico. Recovery of antimony from scrap became a major domestic supply source. Antimony oxide used in flame-proofing compounds for military use became the leading end-product use and necessitated rapid expansion of domestic oxide-smelter capacity.

Demand for consumer products, especially antimonial lead for storage batteries, kept consumption relatively high in the postwar period. The Korean war stimulated consumption in 1951–52, and world production reached record levels. Domestic mine production contributed a significant tonnage, and secondary production continued at a high level.

The post-Korean adjustment of 1953 again curtailed world production and domestic production was essentially terminated. The years following, through 1962, saw world production moving upward to near record levels, secondary production continuing at a high level complementing a large domestic smelter industry supplied by imported ores and byproduct materials, and a relatively stable consumption and market price. Beginning in 1962 increased antimony consumption in the United States and other industry of countries has resulted in a world supply deficit. The unexplained withdrawal of Sino-Soviet supply from free world markets in early 1963 further aggravated the supply situation and price of metal, oxide, and ore reached record levels in 1964 as competition intensified for the available free world supply.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Antimony is produced from ores and as a smelter byproduct in 23 countries located in all continental areas. The predominant sources, however, are China, Republic of South Africa, Bolivia, U.S.S.R., and Yugoslavia which together contributed 85 percent of the estimated world production during 1959–63. The mining of ore primarily for the antimony content is concentrated in relatively small areas and output of the various countries is derived from numerous small, individual operations. The major exception is the Gravelotte mine in the Republic of South Africa which has been the only source of that country's production since 1935. In addition to the ore mined, approximately 30 primary metal smelters and refineries recover antimony as a byproduct in processing nonferrous ores containing small amounts of antimony.

Recovery of antimony in the reclamation of antimonial lead scrap, primarily worn-out storage batteries, is a major source of supply. In the United States, secondary antimony represented 52 percent of the total antimony supply in 1959–63. While secondary recovery is of more significance in the United States due to availability of the proper scrap, it is also a contributing supply in other highly industrialized countries of the world.

The antimony mining industry of the United States is essentially inactive except during periods of abnormally high demand, generally resulting from wartime military requirements and disruption of normal supply. A small annual production is obtained as a byproduct of lead-silver ores and several lead smelters recover byproduct antimonial materials from processing intermediate smelter products. Byproduct antimony represents 13 percent of the primary output and 39 percent of this is derived from imported lead ores and concentrates.

National Lead Co. produces metal from imported Mexican antimony ores at the Laredo, Tex., smelter and oxide from imported African and South American ores at the Charleston, W. Va., plant. American Smelting and Refining Company produces antimonial lead and some oxide at lead refineries in Omaha, Nebr., and Perth Amboy, N.J., Sunshine Mining Co., Kellogg, Idaho, produces an impure cathode metal from locally mined silver-lead concentrates. Antimony oxide from imported ores is produced by Harshaw Chemical Co., McGean Chemical Co., and M & T Chemical, Inc., Foote Mineral Co., McGean Chemical Co., and Hummel Chemical Co. produce small amounts of powdered antimony sulfide. The total average annual production of these companies in recent years has been approximately 12,000 tons of contained antimony.

The antimony consuming industry varies widely in size and end-product utilization. More than 800 companies located in 33 States of the United States consume annually 1 ton or more. Twenty-nine companies consuming over

100 tons annually account for 49 percent of the U.S. consumption and 107 companies consuming 25 tons or more represent 72 percent.

DEFINITIONS OF TERMS, GRADES, AND SPECIFICATIONS

Antimony metal, termed "regulus" is usually marketed in units 10 by 10 by 2½ inches, variously known as blocks, bars, or pigs. Nomenclature in this regard is not fixed. Average weight is approximately 60 pounds to the bar.

Metallic antimony is sold under the brand names of the producing companies. Although a brand name represents a guarantee of antimony content, and frequently of maximum arsenic content, brand names do not denote a fixed analysis of many minor but significant constituents. Purchase contracts are usually written by the seller and include a "typical" analysis that is representative of the material sold under the specified brand name. No samples are taken before delivery; however, analysis is made at the buyer's plant to determine the exact composition of any constituents that are critical to his operation.

The leading domestic brands follow:

(1) National Lead Co.'s RMM brand, which has a guaranteed antimony content of 99.5 percent and a maximum arsenic content of 0.1 percent, and (2) National Lead Co.'s Lone Star brand, which has a guaranteed antimony content of 99.8 percent, arsenic maximum of 0.05 percent, and no other single impurity exceeding 0.1 percent.

Uses of high-purity antimony in the electronics industry led to production of antimony 99.999+ percent pure. The metal carries no brand names. Known producers are Bunker Hill Co., Kellogg, Idaho; Associated Lead Manufacturers, Ltd., London, England; and Mitsui & Co., Ltd., Tokyo, Japan.

Chemical grade ore is that which has a purity sufficient to justify its direct use in production of the oxide, chloride, and other industrial chemical compounds. To qualify as Chemical grade, an ore must have no single metallic impurity greater than 0.1 percent and maximum combined metallic impurities of 0.25 percent.

Liquated antimony sulfide, variously termed "crudum," "crude antimony," or "needle antimony," is marketed on a basis of 70 percent antimony content.

TECHNOLOGY

Geology

Generally, antimony deposits are small, discontinuous bodies having relatively simple geologic relations. Stibnite (Sb_2S_3), together with its oxidized equivalents, is the principal ore mineral. It is found with a limited suite of silicate and carbonate gangue minerals in fissure veins and replacement bodies. The deposits are apparently hydrothermal in origin. Common genetic associations are with granites, granodiorites, and monzonites; however, the enclosing rock walls may be any type traversed by the mineralizing fluids during the ore-forming process. The mineralogy of the veins and their almost invariable shallow depth suggest a low temperature of formation at near-surface positions, possibly related to the configuration of the water table at the time of deposition.

Most of these geologically simple stibnite deposits do not contain more than several thousand tons of ore; nevertheless, the world's most productive antimony mines, including those of Mexico, Bolivia, China, Peru, Yugoslavia, and Algeria are of this type. The economics of their production is often related to (1) minor recoverable values of other ore constituents and (2) locally low mining and transportation costs unrelated to the inherent nature of the deposits.

Antimony also occurs as a constituent of other metalliferous ores. This category ranges in complexity from rather simple deposits in which stibnite is a significant segment of quartz-gold veins to copper-lead-zinc sulfide bodies, in which minor antimony occurs locked within a complex crystal lattice such as tetrahedrite. Virtually all domestic mine output has been from these more complex deposits. In some ore bodies the antimony content shares the total value equally with one or more other metallic constituents of the ore. In many deposits the antimony content of the ore is so small that its presence is detected at some stage in processing so far removed from the mining operation that identity and quantitative relation to specific ore bodies is obscure.

Development, Mining, Milling, and Smelting

Because of the geologic configuration of a typical antimony deposit, entry is by a shallow

shaft or short adit, development by sill cutting in the plane of the vein, and stoping by simple overhand methods between raises driven on the footwall of the ore.

A large-tonnage open-pit mine near Stibnite, Idaho containing disseminated value in gold, antimony, and tungsten was in production before 1953, demonstrating that antimony mining need not be totally confined to small-scale unmechanized methods (*1*).

Commercial ores range from low grades, containing only 1 or 2 percent antimony, to high grades that approach the theoretically pure limit of stibnite, 71.5 percent antimony. The lower grade ores are hand sorted or milled by flotation or simple tabling methods. Owing to friability of stibnite, jigging and dense-medium processes entail prohibitively high slime loss.

Ores and residues containing 5 to 25 percent antimony may be treated directly by roasting to yield the volatile trioxide or the stable, nonvolatile tetroxide. Temperature and quantity of available oxygen determine the kind and relative quantity of the oxide produced. Volatilization roasting may be conducted as an ore concentrating and intermediate smelting process or as a refining method for producing a commercially marketable end product.

Ores containing 45 to 60 percent antimony often are liquated to increase the Sb_2S_3 content, to free the antimony sulfide from associated gangue, and/or to make a directly marketable product. The ore or concentrate is heated in a crucible or reverberatory furnace to a point above the melting point but maintained below the volatilization temperature of stibnite. The fused sulfide descends by gravity through the ore mass and is tapped and collected in a lower container. The resulting material, termed "crudum" or "crude antimony," is used directly in many military and industrial processes (*2*, *4*).

Antimony metal, termed "regulus," is recovered from the trioxide and tetroxide produced in volatilization and dead roasting, from liquated sulfide, from intermediate grades of ores by direct smelting, and from slags and residues produced in refining other metals such as lead. Oxides are reduced most conveniently in reverberatory furnaces, using coke and a suitable flux such as soda ash.

Rich sulfide ore and crudum are reduced to metal by iron precipitation in some localities, as in England, Hungary, Japan, and Mexico (*5*). Fine iron scrap is added to molten antimony sulfide, yielding metallic antimony and iron sulfide. Fluxing produces a low-density iron matte from which the metallic antimony separates by gravity.

Water-jacketed blast furnaces are being used in several modern plants to reduce intermediate (10 to 30 percent) grades of partly oxidized sulfide ores, residues, mattes, and slags. Briquetted flue dust can also be used as a blast-furnace charge. Best conditions are low blast pressure, high smelting column, low antimony content, and proportionally low coke content. Considerable slag is formed and is desirable as it tends to reduce volatilization losses.

At the world's largest antimony smelter, Laredo, Tex., blast-furnace reduction is used prior to reverberatory treatment in producing metal and commercial oxide from oxidized, relatively low grade Mexican concentrates.

The Sunshine Mining Co., Coeur d'Alene district, Idaho, recovers impure cathode metal by electrolysis of an antimony-enriched solution obtained from leaching tetrahedrite concentrate.

Antimony is recovered as a byproduct at lead refineries from processing intermediate metallurgical products that contain antimony as an impurity.

Historically, the purity of antimony has been judged by the appearance of radiating crystal patterns on the surface of the cast. Although impurities may impede this crystal development, the "starring" of the surface is more closely related to the rate of cooling. The false significance of the stars is so firmly established in the minds of antimony buyers, however, that the refiner finds it necessary to star the surface of his castings by slow cooling under cover of a layer of slag (*4*).

USES

Antimony is a brittle, silvery-white metal having a specific gravity of 6.68 and a melting point of 630° C. It is similar in many properties to arsenic and bismuth. Antimony is used both in its metallic form and in the form of compounds, oxides, and salts. Only a small amounts of antimony is used in pure metal end-products. The principal use of metal is as an ingredient in many lead-base alloys and in alloys of other metals. In its nonmetallic form, antimony has a wide range of industrial applications (*3*).

Antimony alloyed with lead finds industrial use in battery grids, chemical pumps and pipes, tank linings, roofing sheets, and cable sheaths. The function of antimony in these antimonial alloys is to increase strength and inhibit chemical corrosion. In antifriction bearings the antimony forms hard crystals of SnSb that are imbedded and dispersed through a soft alloy such as $SnCu_3$ or soft lead. Antimony increases hardness, minimizes shrinkage, permits sharp definition, and lowers the melting point

of printers' type metal. Precision duplication, durability, metallic beauty, and economy make antimonial alloys desirable for decorative castings.

The oxide of antimony, Sb_2O_3, is used extensively in metalware and ceramic enamels and as a white pigment in paints. The trioxide is also a glass former, like silica, and is valued for peculiar light-transmitting characteristics. Various chemical compounds yield pigments of black, vermilion, yellow, and orange. Infrared-reflecting characteristics of a certain antimony sulfide pigment have led to its use in camouflage paints. The pentasulfide of antimony is used in the rubber industry as a vulcanizing agent. The textile industry uses the oxide with chlorinated paraffin and lime as a finishing additive to fibers. The role of the Sb_2O_3 is one of filtering out the fiber-destroying, ultraviolet wavelength of sunlight.

Large quantities of antimony trioxide or trichloride in an organic solvent are used to make military fabrics fire resistant. Flames accompanying initial combustion are restricted or extinguished by chemical reactants released by heat from the treated fabric.

Antimony is used in various ammunition components. Alloyed with lead it hardens small-arms bullets. Tracer bullets have a recess in their base containing a light-emitting antimony sulfide mixture that permits visual tracking of the projectile. Burning antimony sulfide creates a dense white smoke that is used in visual fire control, in sea markers, and in visual signaling. A small but critical tonnage of antimony sulfide is used annually in percussion type ammunition primers as a friction element and heat-transfer medium. High-purity antimony metal is used in increasing amounts in intermetallic compounds by manufacturers of electronic semiconductors and thermoelectric devices.

Industrial consumption of primary antimony in the United States is shown in table 1.

TABLE 1.—*Industrial consumption of primary antimony in the United States, by class of material produced*

[Short tons, antimony content]

Product	1954–58 (average)	1959	1960	1961	1962	1963
Metal products:						
Ammunition	7	(1)	(1)	(1)	(1)	(1)
Antimonial lead [2]	4,823	4,141	4,398	4,708	6,090	6,462
Bearing metal and bearings	862	886	803	737	682	992
Cable covering	177	157	146	141	114	101
Castings	76	84	72	53	64	49
Collapsible tubes and foil	28	33	17	24	112	72
Sheet and pipe	245	202	202	147	127	81
Solder	123	113	130	97	172	188
Type metal [2]	963	883	580	448	429	652
Other	143	130	148	152	271	199
Total [2]	7,447	6,629	6,496	6,507	8,061	8,796
Nonmetal products:						
Ammunition primers	16	11	11	15	14	15
Fireworks	33	28	33	20	23	36
Flameproofing chemicals and compounds	1,017	1,033	1,177	1,138	1,215	1,601
Ceramics and glass	1,777	1,727	1,640	1,223	1,146	1,465
Matches	19	19	17	(1)	9	5
Pigments	1,261	1,167	1,282	845	1,161	1,009
Plastics	790	1,034	1,013	1,228	1,269	1,352
Rubber products	166	217	238	287	460	597
Other	1,684	1,452	1,364	1,434	2,094	1,656
Total	6,763	6,688	6,775	6,190	7,391	7,736
Grand total	14,210	13,317	13,271	12,697	15,452	16,532

[1] Included with "Other" to avoid disclosing individual company confidential data.
[2] Includes antimony content of imported antimonial lead consumed.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

All antimony from domestic sources is a byproduct or coproduct of mining, smelting, and refining other metals and ores that contain relatively small quantities of antimony. Because of the metallurgical affinity of antimony for lead the byproduct material is segregated and extracted at primary lead refineries.

ALTERNATE MATERIALS

Antimony has no properties that make it indispensable, but it has technologic advantages in many areas of application. Mercury, titanium, lead, zinc, chromium, tin, and zirconium may displace antimony in paints, pigments, and enamels. Tin may substitute for antimony in cable sheathings, calcium in battery plates, bismuth in type metal, zinc in decorative cast-

ings, organic synthetics in fireproofing textiles, and copper in bearing metal. However, the choice of a raw material is an economical choice as well as a technological one. Antimony has always been a relatively cheap metal, substituting for more expensive ones. The specific uses, and the extent to which antimony is used, is an economic equilibrium position. With shifts in prices of antimony and of replacing metals there is a corresponding shift in use pattern.

SECONDARY SOURCES AND RECOVERY

Over 50 percent of the annual domestic supply of antimony is derived from scrap. Secondary antimony recovered at 194 plants in 1963 totaled 20,803 short tons valued at $13.5 million at the domestic price of primary metal. Recovery of antimony from battery-plate scrap comprised 60 percent of the total secondary output. Type-metal scrap yielded 3,400 tons of antimony. Bearing-metal scrap contributed most of the remaining feed material. Essentially all secondary antimony was recovered as regenerated antimonial alloys.

The United States has a large quantity of antimonial alloys now in use that will eventually return as scrap to be reprocessed. Consideration of the number of automobiles in use leads to a conservative estimate of 150,000 tons of recoverable antimony available from this source.

RESERVES

The Rocky Mountain and west coast areas of the United States contain numerous small, discontinuous antimony deposits but only a few have been mined successfully when price was exceptionally high or war incentives in effect (*6*). The Federal Geological Survey estimates that ore of this type which could be economically mined largely or entirely for antimony at a required antimony price of 60 cents per pound, contains 55,000 short tons of metal. About half of this resource is in the Yellow Pine district of Idaho.

Currently the only commercial source of antimony in the United States is as a minor by-product associated with the mining and treatment of base and precious metal ores and ultimately recovered at lead smelters. The Geological Survey estimates this type of antimony resource to be 55,000 tons of recoverable metal. The U.S. reserve of mineable antimony at conceivable peacetime prices is 110,000 tons.

There are few commerical deposits of antimony in the world of sufficient magnitude and geological continuity to permit development of significant reserve ore in advance of mining. The deposits found in China, Bolivia, and Mexico are individually of small extent and production is conducted as a small-scale enterprise. The Consolidated Murchison operation in the Transvaal, Republic of South Africa, and the Yellow Pine deposit in Idaho are notable exceptions wherein the mineralized zone is sufficiently large to permit a planned program of mine development and production. World reserves are therefore mainly estimated, and classified as inferred reserves, on the basis of past production, knowledge of area geology, and potential for extension of known ore shoots and new discoveries.

The inferred antimony reserves of the world that are mineable at a price of 60 cents per pound or less are estimated to contain 4.4 million tons of metal. The free world area possesses 1.8 million or 41 percent and the Sino-Soviet bloc, the remaining 2.6 million tons.

Bolivia possesses the largest reserve of antimony in the free world area with an estimated 450,000 tons of contained antimony. Reserves in other countries are as follows: Republic of South Africa, 275,000 tons; Mexico, 225,000 tons; Turkey, 140,000 tons; Australia, 110,000 tons; Yugoslavia, 110,000 tons and Peru, 70,000 tons. Algeria and Canada have an estimated 55,000 tons and collectively the other free world countries contain 200,000 tons.

China is conservatively estimated to contain 2.2 million tons of contained antimony in reserves centered in Hunan Province and has by far the largest antimony resource in the world. Reserves of the U.S.S.R. are estimated at 275,000 tons; Czechoslovakia, 55,000 tons; and Hungary, 25,000 tons.

CONSERVATION PRACTICES

The high volatilization losses attending ore smelting are for the most part compensated by recirculating the entrapped flue dusts.

Lead smelters recover antimony metal, oxide, and antimonial lead from intermediate smelter products, such as slags, drosses, flue dusts, and residues generated at copper, lead, tin, and tungsten smelters.

Users of antimonial alloys, such as battery, bearing, and type-metal manufacturers recirculate new and used scrap metal. Primary refineries use varying amounts of scrap in addition to ores, concentrates, and intermediate smelter products.

SOURCES OF STATISTICAL INFORMATION

Data on production, consumption, and stocks of primary antimony are collected and tabulated quarterly by the Bureau of Mines. The Department of State through its Foreign Service reports furnishes statistics relating to the antimony industry in foreign countries. There are numerous foreign publications that give fragmental statistics on foreign production and consumption. Import and export statistics are obtained from Department of Commerce, Bureau of the Census.

PRODUCTION, CONSUMPTION, AND TRADE

World production of primary antimony is approximately 60,000 tons annually. Of this total China is the leading producer followed by Republic of South Africa, Bolivia, U.S.S.R., Mexico, Yugoslavia, and Turkey. The free world contributed about 60 percent in 1963 and the Sino-Soviet bloc the remaining 40 percent. This supply is augmented in the industrialized countries by reclamation of antimonial scrap. Of the countries in the world that produce antimony ores, only a few have exportable surpluses. Some approach self-sufficiency, whereas others must supplement their domestic output with imports of varying quantities of ore, metal, and oxide. Many countries produce no antimony and depend entirely upon imports to satisfy domestic requirements. The United States requires over 20 percent of the world's primary output. Other principal consuming countries are United Kingdom, U.S.S.R., France, Belgium, Japan, West Germany, and Italy.

Yearly smelter production in the United States is about 33,000 tons including 21,000 tons of antimony in alloys recovered from scrap. Of the 12,000 tons of primary smelter output, approximately 75 percent comes from imported ores and concentrates and 25 percent from by-product materials segregated in refining lead bullion and other intermediate metallurgical products derived from both foreign and domestic ores.

Industrial consumption of antimony in the United States is approximately 36,000 tons. Of this some 55 percent is recovered from scrap and reused in the form of antimonial lead. An additional 4 percent is recovered at lead primary smelters largely in the form of antimonial lead. The remaining 41 percent is recovered from antimony ores, of which 70 percent is derived from domestic smelter production, and the remainder is imported metal and oxide. The salient statistics of domestic antimony are shown in table 2.

In recent years China, Republic of South Africa, Mexico, and Bolivia have been the major suppliers of ore to the world's industrial areas. Mexico and the Republic of South Africa are the major suppliers of ore to the United States with each contributing about 40 percent of the total. South America, principally Bolivia, contributes essentially all of the remaining 20 percent. Metal and oxide imports come chiefly from Yugoslavia, United Kingdom and Belgium-Luxembourg. Both the United Kingdom and Belgium-Luxembourg have large smelter capacity, fed entirely by imported ores. They produce metal and oxide primarily to supply internal and European needs, but surpluses are sold in the U.S. market. Yugoslavia, however, has an ore reserve base that supplies its smelters.

Imports of all categories of antimony totaled 17,800 tons in 1963 of which approximately 56 percent was as antimony in ore for domestic refining, 30 percent was as refined metal and 14 percent as refined antimony oxide. Exports of antimony constitutes a relatively insignificant tonnage usually in the form of metal and alloys in crude form.

TABLE 2.—*Salient antimony statistics*

[Short tons]

	1954–58 (average)	1959	1960	1961	1962	1963
United States:						
Production:						
Primary:						
Mine	681	678	635	689	631	645
Smelter [1]	10,447	8,748	9,954	11,329	11,727	12,117
Secondary	22,449	20,043	20,104	19,466	19,362	20,803
Imports, general (antimony content)	12,541	13,273	14,519	13,942	16,833	17,781
Exports	95	174	906	44	45	143
Consumption [2]	14,210	13,317	13,271	12,697	15,452	16,532
Price: New York, average cents per pound	32.89	31.30	31.30	33.89	34.75	34.75
World: Production	54,400	58,700	58,800	57,400	58,700	61,100

[1] Includes primary content of antimonial lead produced at primary lead smelters.
[2] Includes primary content of antimonial lead produced at primary lead smelters and antimony content of alloys imported.

Ore and concentrates enter the United States duty free. Imports of metal are dutiable at the rate of 2 cents per pound; oxide, 1 cent; and liquated sulfide, one-quarter cent per pound.

SELF-SUFFICIENCY AND STRATEGIC CONSIDERATIONS

About 88 percent of the U.S. smelter output of primary antimony is derived from imported antimony ores and concentrates. An additional 6 percent is recovered from foreign metalliferous ores and intermediate smelter products at domestic lead refineries. Thus, it is evident that domestic smelters are over 93 percent dependent on foreign ores. Moreover, U.S. dependency does not end with the acquisition of smelter feed. In 1963, 45 percent of the domestic supply of metal, oxide, and sulfide was imported. In summary, approximately 93 percent of the total supply of primary antimony available in the United States in 1963 originated in foreign ores.

The two factors that combine to classify antimony as a strategic material are (1) the nearly complete dependency of the United States on foreign supply and (2) important military uses in flameproofing compounds, camouflage and fire-retardant paints, ammunition components, and bearings and batteries.

The erection of the Laredo, Tex., smelter in 1930 and the restriction of Chinese shipments after the Japanese conquest in 1937 shifted the source of U.S. imports of ore chiefly to Mexico, where concentrates are now transported by rail. Expansion of mining in Bolivia during World War II further strengthened the U.S. ore supply position from Western Hemisphere sources. However, the large supplementary requirements for antimony in metal and oxide, as well as contributory quantities of ore, continue to come from distant overseas sources.

GOVERNMENT PROGRAMS

Under various congressional authorizations in times of national need the Government has stockpiled antimony, controlled prices, allocated supply, and explored for domestic ore deposits. During World War II, the Reconstruction Finance Corporation and the Metals Reserve Company procured stocks of strategic and critical materials, including antimony, from China, Mexico, and Bolivia. Under the Strategic Minerals Act, the Bureau of Mines successfully conducted ore-research projects that augmented domestic antimony resources. The Office of Price Stabilization administered pricing during the Korean conflict, and the Defense Minerals Exploration Administration was inaugurated to grant loans to private industry for approved exploration.

Government inventories of antimony totaled 52,985 tons on June 30, 1964, of which 30,275 tons was in the national (strategic) stockpile, 444 tons in CCC stocks, and 22,226 tons in the supplemental stockpile. Redetermination of stockpile objective under the Strategic Minerals Act by the Office of Emergency Planning in 1964 resulted in approximately 50 percent of this inventory being declared surplus to the mobilization requirements of the United States. Under Public Law 88–615, signed by the President on October 2, 1964, sale of 5,000 tons of this surplus was authorized to assist in alleviating a developing industrial supply shortage. The initial sale to domestic producers and consumers was made in November 1964 and the remainder offered in subsequent sales in late 1964 and 1965.

PRICES

Since 1900, the market price of antimony has been characterized by abrupt fluctuations due to (1) the wide difference between peacetime and wartime demands, (2) availability of low-cost Chinese antimony sufficient to supply a large portion of peacetime demand, and (3) the high-cost incentive required to meet wartime demand. Price has thus seen a low of 4 cents per pound in 1922 and a high of 52 cents in 1951.

The most recent low price for 99.5 percent, domestic-brand metal f.o.b. New York in bulk was 31.5 cents per pound established in February 1958. An increase to 34.75 cents in April 1961 was held until January 29, 1964. The developing shortage of metal throughout the free world then initiated a succession of price increases to a quoted price of 45.75 cents per pound in early October 1964.

The scarcity of ores for smelter feed both foreign and domestic has resulted in a major price increase in relation to the stability prior to early 1963. Imported ores have increased from a range of 16 to 24 cents per pound of contained antimony, dependent on impurities contained and grade, to a early October 1964, quoted range of 41 to 47 cents per pound delivered in New York. Antimony trioxide priced at 30 cents per pound in early 1963 had risen to 60 cents per pound delivered in carload lots by early October 1964.

TAXES

Depletion allowance to domestic antimony miners is 23 percent. Domestic companies owning foreign antimony mines that are an integral

part of their domestic facilities may receive a 15-percent depletion allowance.

TRANSPORTATION

Transportation cost is a limiting consideration in many antimony mining districts of the world, often representing more than one-third of total value of the concentrate, especially during periods of abundant supply. Estimated cost to move a ton of Bolivian antimony ore concentrates from the millsite to New York is $57. A ton of concentrates from Consolidated Murchison mines in the Republic of South Africa can be shipped to New York for approximately $42 per ton. Average gross value of a ton of antimony concentrates early in 1959 was approximately $135 but by late 1964 it had increased to about $550. Low-grade Mexican ore is shipped exclusively by rail to the National Lead Co. smelter at Laredo, Tex. Bolivian ore comes to the United States from the Chilean port of Arica and the Peruvian port of Mollendo, then by sea freight to the port of entry. The Republic of South Africa ore is freighted by rail to Lourenço Marques in Mozambique and by ship to Liverpool, Portsmouth, and New York.

RESEARCH

Research by the antimony producing industry primarily concerns the development and expansion of markets. In a project sponsored by a domestic mining company, Battelle Memorial Institute has recently done notable work on developing indium-antimony and aluminum-antimony semiconductors and on the infrared transmission characteristics of antimonial glass. Two domestic producers are now experimenting in the production and characteristics of superpure antimony metal for the electronics industry.

Research by the consuming industry is more specialized, being confined to developments that meet a specific industrial need. American Electroplaters Society, Radio Corp. of America, and others have recently published work on electroplating of antimonial alloys. Several chemical companies conduct continuous research on the properties and applications of the pigments, glasses, and glazes.

The Department of Agriculture has done research for the military aimed at developing a more useful fire retardant. U.S Naval Engineering Experimental Station has recently worked on improving antimonial-bronze bearing alloys.

The Bureau of Mines conducted research on the hydrometallurgy of antimony-bearing ores of the Coeur d'Alene district, Idaho, in an attempt to establish a more economical technique of recovering antimony from complex ores. Alaskan mercury-antimony ores were also studied by the Bureau of Mines to determine the technology and economics of separating the two principal ore constituents by fluidized-bed roasting of a bulk concentrate. In this process the mercury content is volatilized, and antimony is recovered from the residual calcine.

OUTLOOK

Antimony has a specialized consumption pattern which has not conformed to general economic patterns but rather to specific factors associated with storage batteries, textiles, plastics, and rubber. Expanding requirements in these applications are indicated to overbalance decline in some historical uses. The U.S.-required peacetime annual supply of antimony is therefore estimated to increase by some 2 percent annually to approximately 46,000 tons in 1970.

The geological and economic factors associated with the domestic antimony deposits precludes successful competition with peacetime imports and discourages hope for significant domestic output even under the incentives of an abnormally high price. Byproduct antimony is dependent on the market for the major valued constituents but the ratio of antimony to other metals is so small that only a moderate increase to 3,000 tons is forseen in the expanded production of associated metals.

Availability of antimonial scrap imposes a comparative inflexibility to secondary recovery of antimony in antimonial-lead. Improved lead price will bring out additional scrap but not on a sustained basis. Secondary supply of antimony is therefore believed relatively stable at 21,000 tons per year.

The 22,000 tons of primary antimony required in addition to domestic supply will be necessarily obtained as imports. Imports of ore to supply the domestic smelters and refiners of metal and oxide will be predominately from Mexico, Bolivia, and the Republic of South Africa with supplemental supply from Peru, Brazil, and Guatemala. Metal and oxide will be supplied principally by Yugoslavia, United Kingdom, Belgium-Luxembourg, Mexico, and Thailand.

PROBLEMS

The basic problem of the antimony industry is the assurance of an adequate supply to meet a rising world demand and, especially, to meet sharply fluctuating demand for new metal resulting from the wide difference in peacetime requirements and those of wartime. General geographic separation of the producing and consuming areas, lack of large, integrated mining establishments in most of the producing areas and dependence on the low-cost output of China has prevented a stable coordination of supply and demand.

Continuing depletion of high-grade ore in Mexico, Bolivia, and the Republic of South Africa is a problem necessitating adjustments in smelting practices and increase in production cost. This particularly affects the production of oxide directly from higher grade ores free of contaminating impurities.

The U.S. supply problem arises in part from the fact that presently known domestic antimony deposits are of small potential and uneconomical in competition with foreign production under normal market conditions. Thus the presence or potential of overwhelming foreign production availability is a deterrent to large scale exploration and development of domestic resources.

The consuming industry is faced with continuing problems in maintaining technological as well as economical advantages in applications of antimony in competition with other metals and organic synthetics.

The concentration of economically mineable antimony resources in a relatively few major areas of the world predicates continued dependence on these sources in an expanding industrial economy. Production and marketing policies of the centrally planned economics constituting the Sino-Soviet bloc will undoubtedly continue to be a disruptive factor in free world supply and, also, a deterrent to development of supplemental sources of supply. Depletion of easily mined, direct shipping ores of Bolivia, Mexico, and Republic of South Africa and the difficulties of development of additional sources to augment production predicates an increasingly tight supply and competition for available ores to meet international requirements for primary metal and oxide.

The price of antimony will reflect the rising cost of production and beneficiation of lower quality ores and market competition and is foreseen as unstable and substantially above that previously considered normal in peacetime.

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ARSENIC

By Arnold M. Lansche [1]

ARSENIC TRIOXIDE or arsenious oxide (As_2O_3), is the most common compound of arsenic and in commerce is often called white arsenic. In the United States, white arsenic is produced principally as a byproduct of copper and lead smelting and in the recovery of other metals, notably gold and silver.

White arsenic is used principally for manufacturing calcium and lead arsenate insecticides. However, the usually unpredictable changes in insect infestation and the development of temporary immunities to insecticides among pests make the demand for arsenical insecticides unstable. This irregularity of demand is one of the basic problems of the arsenic industry. Other important uses of white arsenic are in wood preservatives, lead shot, glass, and weed control.

The use of arsenicals as insecticides has declined sharply since the advent of organic insecticides. The once popular lead and calcium arsenates have been largely replaced by organic compounds, such as dichlorodiphenyltrichloroethane (DDT), benzene hexachloride (BHC), toxaphene, and organic phosphate compounds, which have caused serious economic problems to manufacturers of arsenicals.

The United States is the world's second largest producer and largest consumer of white arsenic, producing about one-fourth and consuming nearly one-half of the world total.

The United States is in a favorable position to meet its white arsenic requirements. It is unlikely that any new uses for arsenic or its compounds will tax the existing resources or producing capacity of the Nation.

Research to develop the usefulness of arsenic has greatly increased, and several promising avenues have been opened which may lead to expanded use for both the metal and its compounds.

BACKGROUND

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Copper ores are the primary source of arsenic. Since 1926, Sweden and the United States have been the chief producers of white arsenic, with Sweden supplying about 23 percent of the total. In Sweden the compound has been produced by Boliden Mining Co., while the Anaconda Company at Anaconda, Mont., and American Smelting and Refining Company at Tacoma, Wash., produce white arsenic in the United States.

In 1963, 13 countries provided quantitative data on the production of white arsenic. Nine other countries are thought to have produced, but too little information was available to estimate production.

White arsenic is produced in five of the continents. Nations that produce the compound in North America are Canada, Mexico, and the United States. Brazil and Peru are the producing countries of South America; Argentina may produce some. In Europe the producers are Belgium, France, West Germany, Portugal, Spain, and Sweden; Greece and Italy did not report output in 1963; Austria, Czechoslovakia, East Germany, Finland, Hungary, and the United Kingdom may also produce some. Japan is the only reporting producer in Asia, but it is very likely that the U.S.S.R. and China produce white arsenic. Southern Rhodesia produces the compound in Africa.

DEFINITIONS OF TERMS, GRADES, AND SPECIFICATIONS

Prime white arsenic (As_2O_3) is a fine, white powder. Commercial specifications require that the refined product contain 99 percent or more

[1] Commodity specialist.

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of arsenic trioxide; usually it contains 99.5 percent. It should be free from lumps, and for some uses a certain standard of solubility in nitric acid may be specified. Crude arsenic is grayish white, and sales contracts generally specify 95 to 98 percent arsenic trioxide. For sale to large consumers who buy in carlots, white arsenic is shipped in bulk and also packed in barrels containing 600 to 650 pounds each. For jobbing it is packed in casks of 100 pounds or more, and for the retail trade it is sold in packages of 1 to 10 pounds. Other important commercial compounds are arsenates or salts of arsenic acid. Both the arsenites and arsenates, except those of the alkali and alkaline-earth metals, are almost insoluble in water but are readily dissolved by acids.

TECHNOLOGY

Arsenic is not an abundant element. The average content of arsenic in the lithosphere compares with that of tin; however, it is widespread in occurrence. The arsenic concentration in sea water of 0.02 milligram per liter exceeds that of iron. The minerals realgar, orpiment, and arsenopyrite are more abundant. However, the most extensive mineralogical occurrence of arsenic is associated with copper, lead, cobalt, nickel, iron, and silver, either alone or with sulfur. The average arsenic content of igneous rock is reported to be 5 grams per ton (*11*).[2] Significant arsenic is found in the phosphate (mainly apatite) components of igneous rocks. Native arsenic occurs in some mineral veins. It is a general rule that arsenic begins to separate at the highest temperatures after the main stage of crystallization; that is, during the pegmatitic stage. Thus arsenic minerals are found in small quantities in deposits formed during the early and main stages of magmatic crystallization. In the late magmatic crystallites, arsenic is strongly concentrated in arsenopyrite (FeAsS), and loellingite ($FeAs_2$). Magmatic sulfides average about 2,000 grams of arsenic per ton. Pneumatolytic and hydrothermal deposits contain the greatest number of independent arsenic minerals.

Since most arsenic is produced as the oxide (white arsenic), a byproduct of the smelting of other metals, the metallurgy of arsenic is concerned chiefly with the treatment of arsenic-bearing flue dusts from smelting plants to recover the arsenic content as either crude or refined white arsenic. The crude flue dust, carrying as much as 30 percent arsenic trioxide, is mixed with a small quantity of pyrite or galena and roasted in a reverberatory furnace. The pyrite or galena prevents formation of an arsenite during roasting, producing a clinkering residue suitable for return to the process for recovery of other metals. The gases from the roasting furnace, containing the volatilized arsenious oxide, are cooled by passing them through a series of brick chambers or kitchens, in which the temperature ranges from 220° C. in the first chamber to 100° C. or less in the last. In this cooling process the arsenious oxide condenses as crude white arsenic and is collected in cooling flues, baghouses, or Cottrell precipitators. Much of the product is used in the crude form, but if a higher purity is required the operation is repeated to yield a product assaying 99 percent or more arsenic trioxide.

Metallic arsenic is prepared from white arsenic by reduction with charcoal. A 200- to 450-pound batch of white arsenic and charcoal is charged to a furnace where reduction takes place at about 1,200° to 1,300° F.

USES

White arsenic is the major ingredient in the United States in the manufacture of the arsenical insecticides, calcium arsenate and lead arsenate. The once popular paris green (copper acetoarsenite) insecticide is now of minor importance. Calcium arsenate is more effective than lead arsenate in combating the cotton boll weevil. Lead arsenate is used chiefly in poison sprays and dusts for destroying the coddling moth, plum curculio, cabbageworm, potato bug, tobacco hornworm, and pests that injure fruits and vegetables. Calcium arsenate and lead arsenate supply arsenic to agriculture in a form that will not injure plants but will destroy insects that eat plant leaves.

White arsenic alone or mixed with other substances is used as a wood preservative. Wolman salts (25 percent sodium arsenate) is a major wood preservative. Other wood preservatives include chemonite, and ammoniacal copper arsenite which has a composition prescribed by Federal Specification TT–W–549 to contain 1.84 percent cupric hydroxide $Cu(OH)_2$, 1.3 percent As_2O_3, 2.8 percent ammonia, 0.05 percent acetic acid and water. Greensalt is a chromated copper arsenate. There are three "Bolidensalts." "Bolidensalt" BIS is the trade name for zinc-chromium arsenate which has the approximate composition 20 percent arsenic acid H_3AsO_4, 19 percent mono-hydrogen sodium orthoarsenate $Na_2Cr_2O_7 \cdot 2H_2O$, 16 percent sodium dichromate, and 43 percent zinc sulphate, $ZnSO_4 \cdot 7H_2O$; the mixture is used in a water solution in wood preservative plants, and is applied to the wood under vacuum and pressure. The zinc and chromium arsenates are precipitated in the

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

wood fibers, making the treated wood resistant to leaching. The mixture of zinc and copper arsenates with sodium dichromate is trade-named "Bolidensalt" BIS Copperized and is used in the same way as "Bolidensalt" BIS. The copperized mixture has the following approximate composition: 20 percent H_3AsO_4, 19 percent Na_2HAsO_4, 16 percent $Na_2Cr_2O_7 \cdot 2H_2O$, 22 percent $ZnSO_4 \cdot 7H_2O$, and 22 percent copper sulfate, $CuSO_4 \cdot 5H_2O$. "Bolidensalt" K33 is the trade name for nonionic copper-chromium arsenate which has the following approximate composition: 34 percent arsenic pentaoxide, As_2O_5; 26.6 percent chromium trioxide, CrO_3; 14.8 percent cupric oxide, CuO; and 24.6 percent water. The nonionic arsenate is used to preserve wood in wooden cooling towers and other wooden structures subject to rot and in high-transmission-line poles because the electrical resistance of wood is increased. All ingredients in the nonionic arsenate are almost completely fixed in the wood, and no soluble by-products are formed. The arsenate is effective against all wood destroyers including soft-rot organisms. Another wood preserver, Osmosalts, is a mixture of 34 percent sodium fluoride, NaF; 25 percent sodium arsenate; 34 percent $Na_2Cr_2O_7$; and 7 percent dinitrophenol.

White arsenic is one of the most practical and persistent materials for permanent soil sterilization and has distinct advantages over soluble arsenic compounds used for this purpose.

Sodium arsenite is the active ingredient of herbicides used as weedkillers and to control aquatic plant life. It is used to some extent for sheep and cattle dips and for termite control.

The only extensive use of white arsenic not based on its poisonous quality is in glassmaking. A substantial quantity of the domestic output has been used as a decolorizer, as a constituent of opalescent and opal glass, and in enamels.

Probably the most familiar metallurgical application of arsenic is in manufacturing lead shot. Small additions of arsenic, up to 1 percent, change the surface tension of lead and permit the formation of spherical shot. Arsenic is used to improve particular properties of lead, copper, and some of their alloys. Additions of small amounts harden lead and minimize softening of lead-base-bearing alloys used in internal-combustion engines where elevated temperatures are encountered. Arsenical lead babbitts develop remarkably fine and uniform structure and have excellent fatigue strength.

An important metallurgical use of arsenic is in arsenical copper, where it increases corrosion and erosion resistance, raises the annealing temperature, and perhaps serves as a deoxidizer. Arsenical copper is useful in making automobile radiators and other manufactured objects assembled by soldering, because little or no strength is lost from soldering heats owing to the higher annealing (recrystallization) temperature.

Two leading commercial sulfides of arsenic are arsenic disulfide (As_2S_2), an orange-red compound found in nature as the mineral realgar but ordinarily made artificially, which contains 70 percent arsenic; and arsenic trisulfide (As_2S_3), a lemon-yellow material containing 61 percent arsenic and found in nature as orpiment or manufactured artificially. Realgar is used as a paint pigment, as a depilatory in tanning, and for making a white (Bengal) fire used in pyrotechnics. The red color is a desirable feature in treating hides or skins, but as sodium sulfide and calcium compounds are cheaper and nonpoisonous, they tend to displace arsenic sulfide for this use. Orpiment, or king's yellow, is used as a paint pigment and a reducing agent in chemical work. It is very bright yellow and has good covering power but is not permanent when exposed to light and cannot be mixed with many other colors. The pentasulfide (As_2S_5) has a more limited use in paint pigments, blue fire, and Bengal lights.

In medicine, arsenic sulfides and other arsenical compounds have been prescribed for centuries for many diseases, without true success. Fowler's solution, a 1-percent aqueous solution of potassium arsenite, introduced late in the 18th century, is considered to be the first really effective arsenical drug. It is dispensed today for certain human skin disorders and for animal therapy.

Gallium arsenide, gallium arsenide phosphide, indium arsenide, and indium-gallium arsenide have been used on a very small scale as diode components of masers and lasers which have a high efficiency in converting electric energy into infrared radiation.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Arsenic occurs principally as a component of various metallic ores in which it is an undesirable impurity. The domestic output is obtained as a byproduct from the smelting or roasting of these ores for recovery of other metals, mainly gold, silver, copper, and lead. Often the arsenic content of the treated ores is very small. At many custom mills and smelters arsenic has been classed as a nuisance material.

ALTERNATE MATERIALS

DDT (dichlorodiphenyltrichloroethane) continues to be the most popular individual chlorinated hydrocarbon substitute for copper arsenate and lead arsenate. A group of chlorinated hydrocarbons, including aldrin, chlordane, dieldrin, endrin, heptachlor, and toxaphene, have grown rapidly in demand as substitutes for the arsenates; production of the arsenates was almost stationary in comparison. The organic phosphorus compounds malathion and parathion also were available as substitutes for the arsenates. About as much parathion as copper arsenate was produced in the period.

It has been claimed that most of the alternate materials have lower toxicities for humans than the inorganic arsenates; in October 1959, in the United Kingdom, the British Weed Control Council (*5*) recommended that manufacturers stop making arsenical sprays. However, in 1962, Carson (*3*) discussed at some length the toxicity of the arsenicals and suggested that the relatively new organic poisons are more deadly.

RESERVES

White arsenic reserves were estimated to be 2.5 million short tons in 1963. The wide occurrence of arsenic in ores of ferrous metals and nonferrous base metals implies that the arsenic supply is indefinite but directly related to output of metals in those two groups. Gold and silver ores are often associated with arsenic as arsenopyrite, orpiment, and realgar and contain large reserves of arsenic. The Getchell mine in Nevada began mining gold in June 1962, and the arsenic sulfide content was oxidized to white arsenic and sent to the arsenic waste ponds (*7*).

Data on foreign reserves were not available through 1963. It is unlikely that arsenic reserves in foreign countries will be available on a reliable basis in the near future because of the small demand.

SOURCES OF STATISTICAL INFORMATION

Production, sales, and stocks of white arsenic are voluntarily reported annually to the Bureau of Mines by domestic producers, but are withheld from publication to avoid disclosing individual company confidential information. Annual U.S. production of calcium and lead arsenates are obtained by the U.S. Department of Commerce, and similar information regarding the consumption of wood preservatives is obtained by the Forest Service, U.S. Department of Agriculture. White arsenic export data are not available. Imports of both white and metallic arsenic are available from records of the U.S. Department of Commerce.

PRODUCTION, CONSUMPTION, AND TRADE

Arsenic metal has not been produced in the United States since 1950. Production information about white arsenic in the United States has not been made public since 1959 because output has come from only two companies, The Anaconda Company at Anaconda, Mont., and American Smelting and Refining Company at Tacoma, Wash. In 1959 production of white arsenic was 5,189 short tons.

Mexico has been for many years the principal source of white arsenic imported by the United States. Mexico supplied 73 percent in 1963, France 14 percent, Sweden 12 percent, and Canada 1 percent. During 1959–63 white arsenic was occasionally received from the Netherlands, Poland-Danzig, Portugal, and the United Kingdom. There was 169 short tons of metallic arsenic imported for consumption in 1963.

Exports of white arsenic from the United States have not been reported by producers since 1947. Calcium arsenate and lead arsenate were exported in small quantities.

White arsenic, arsenic sulfide, and sheepdip are duty free. The duty on arsenic acid is 3 cents per pound. The duty on metallic arsenic was continued at 2.5 cents per pound when other rates were changed on August 31, 1963; paris green was removed from the free list, and the duty became 10.25 to 25 percent ad valorem; lead arsenate duty became 1.5 to 3 cents per pound; and compounds of arsenic not specified in the Tariff Act of 1930 were changed from a duty of 21.5 percent of their foreign market value to 10.5 to 25 percent ad valorem. The higher duties applied to Communist nations.

STRATEGIC CONSIDERATIONS

The production of white arsenic as a byproduct of copper and lead smelting has been so great that supply usually exceeds demand. The reserves of arsenic in the United States are adequate for all forseeable requirements. The output of white arsenic is entirely from Washington and Montana.

PRICES

Since February 9, 1961, the price of refined white arsenic has been stable at 4 cents per pound at New York docks (powdered, in barrels, carlots). The quotation for white arsenic,

f.o.b. Laredo, Tex. (the major port of entry), remained 4.5 cents per pound throughout 1958–60; on February 9, 1961, the price increased to 5.1 cents, where it remained throughout 1963. The bulk price of crude white arsenic was 2.6 cents per pound at both Laredo, Tex., and Tacoma, Wash. at the end of 1963; the barrel price at Tacoma was 4.2 cents per pound.

The Oil, Paint and Drug Reporter quoted the price per pound (carlots) of calcium arsenate from September 15, 1958, to October 3, 1960, at 9 to 9.24 cents; since then the price has not been quoted. Lead arsenate in 3-pound bags (carlots) declined from 27.5 cents per pound to 26.25 cents November 3, 1958, where it remained until March 30, 1959; on April 6 the quotation was 30.5 cents which held through January 22, 1962; on January 29 the quotation was 26 cents, at which it remained through 1962 and 1963.

There is no domestic price for arsenic metal.

TRANSPORTATION

White arsenic can be shipped in bulk (carlots) in covered hopper cars and in covered motor vehicles. Shipments are made in wooden barrels or kegs, or packed in portable, collapsible, rubber containers not over 70 cubic feet in capacity, as approved by the Bureau of Explosives. The rubber containers are authorized only for carload or truckload shipments. White arsenic can be imported in strong, siftproof, waterproof cloth containers, packed in metal-strapped wooden boxes. For jobbing white arsenic is packed in casks of 100 pounds, and for the retail trade it is sold in packages of 1 to 5 pounds.

Arsenic metal usually is shipped in lumps in sealed iron drums or kegs containing a maximum of 200 pounds.

Arsenic metal, white arsenic, arsenic acid, lead arsenate, calcium arsenate, and other arsenicals are classed as dangerous articles and must be packed, marked, certified, labeled, and described according to the Interstate Commerce Commission Code of Federal Regulations, title 49, part 71–90, section 72.5, for Class B Poisons, January 1, 1963 (Revised).

RESEARCH

As a result of research by industry, a method was patented for removing arsenic from complex ores of cobalt and nickel (*13*). Gallium arsenide single crystals have been grown on substrates of germanium, molybdenum, and tungsten (*1*, *12*). A diode was described for maser or laser operation (*8*). Tests were made by industry to evaluate cacodylic acid [$(CH_3)_2$-AsOOH] as a cotton plant defoliant and dessicater (*4*).

The Metallurgical Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers published several papers which discussed the crystal growth, junction preparation, electrical, chemical, and optical properties of gallium arsenide phosphide and gallium arsenide (*2*, *6*, *9–10*, *14*).

OUTLOOK

The short-term outlook is for world production of white arsenic to continue at the 1959–63 level. The long-term outlook is one of steady supply closely tied to copper, lead, and zinc smelting, and to gold and silver production.

Research has brightened the prospects for greater consumption of arsenic in all of its old uses and has opened up new, small scale applications in maser and laser devices.

PROBLEMS

A basic problem of the arsenic industry is the highly fluctuating demand for arsenical insecticides, the principal market for white arsenic.

A marketing problem exists in the consumers' resistance to use of arsenical insecticides and weedkillers when other products are available.

Owing to its byproduct relationship to other metals, particulary copper and lead, production of white arsenic cannot be readily adjusted to highly fluctuating demand.

Lacking large-scale consumer markets, producers are frequently faced with the problems of disposal or augmenting storage facilities for a bulky and poisonous material.

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ASBESTOS

By Timothy C. May [1]

ALTHOUGH asbestos has been known and used for at least 2,000 years, it was not until the end of the 17th century that it began to be regarded as something other than an object of superstition. It possesses some of the characteristics of the animal, vegetable, and mineral kingdoms. Although crude asbestos is naturally a dense mineral, it can be processed into a material as light, buoyant, and feathery as thistledown, which can be woven like cotton or wool.

Asbestos is a name applied to a group of naturally fibrous minerals. The largest producers of asbestos are Canada and the U.S.S.R. The United States is the largest consumer but produces only a small part of its requirements. The major part of the U.S. supply of chrysotile is imported from Canada. Most crocidolite and all amosite used in the United States are produced in the Republic of South Africa. Low-iron long-fiber chrysotile and amosite are important in defense purposes. Crocidolite has important industrial uses that are less directly related to defense problems. During World War II and several years thereafter, most grades of good quality asbestos were in short supply. The discovery of a large deposit of suitable low-iron chrysotile in British Columbia, Canada, relieved the short supply situation. The production and consumption of asbestos should continue to increase. The principal suppliers of U.S. markets—Canada and the Republic of South Africa—appear to have adequate reserves of asbestos to meet requirements for many years at current rates of consumption.

An important problem in asbestos is the complete dependence of the United States on foreign sources of supply. Other problems are the lack of a commercially satisfactory substitute for amosite, current lack of interchangeability of the various types of asbestos, waste disposal, and biological effects of asbestos upon the industrial employee.

BACKGROUND

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

The United States leads in manufacturing asbestos products and consumes 23 percent of the world asbestos production; however, domestic sources furnish only 9 percent of the raw asbestos needed. Most of the supply is obtained in Canada, but important quantities, particularly of special kinds and grades, originate in the Republic of South Africa (*4–5*).[2]

The Province of Quebec, Canada, has the largest mines and mills in the world. The U.S.S.R. rivals Canada as an important producer. The Republic of South Africa, Southern Rhodesia, Swaziland, Italy, and the United States are substantial producers, and smaller supplies originate in many countries. The variety chrysotile constitutes about 95 percent of the world supply, and unless otherwise designated the data herein relate to chrysotile.

Total world production in 1963 was 3.2 million short tons of all grades and varieties. Of this total, Canada produced about 40 percent, the U.S.S.R. 38 percent (estimated), the Republic of South Africa 6 percent, Southern Rhodesia 4 percent, the United States 2 percent, Italy 2 percent, and Swaziland 1 percent.

Prior to 1962, the only large production of asbestos in the United States was from a deposit in Eden and Lowell Townships, Vt., in what is regarded as a southern extension of the

[1] Commodity specialist.
[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

Quebec deposits. In 1963, deposits in the Copperopolis, Coalinga, and Napa areas in California began production, and in the next few years their combined production is expected to exceed that of Vermont. Several operators have small chrysotile mines in an area about 60 miles long and 25 miles wide in the Salt River and Cherry Creek basins of Gila County, north of Globe, Ariz. These are the only sources of chrysotile asbestos that have been developed in the United States. Chrysotile deposits are known in Montana, Wyoming, and other States, but production has been negligible. In addition, amphibole asbestos is produced sporadically in North Carolina and Georgia (*6–8, 16, 20–21, 25–27*).

The largest known asbestos deposits in the free world are in an area 75 miles long by 5 or 6 miles wide between Danville and the Chaudière River Valley, in the Province of Quebec, Canada. Eight companies are actively engaged in mining in this area. Six of these are subsidiaries of companies that operate large asbestos-products plants in the United States. Deposits occur elsewhere in Canada. Asbestos was mined in Munro Township, 12 miles east of Matheson, Ontario, from 1950 until the mine closed down on July 31, 1964. Asbestos has been mined continuously in northern British Columbia since 1953. In mid-1963 a new mine began operating at Baie Verte in Newfoundland. An important deposit in the northern Ungava region of Quebec is being examined and may be considered a prospective producer. Canadian production in 1963 was valued at Can-$135 million, whereas U.S. production had a sales value of about $5 million.

The Soviet deposits, situated in the Bajenova district of the Urals, are extensive. The mines and mills are large, and most of the fiber is used within the country in the manufacture of various asbestos products.

Southern Rhodesia is an important producer of chrysotile asbestos, particularly in the Shabani area. The fiber from these deposits has such a low iron content that it can be made into the excellent electrical insulating material that is required in the construction of electric cables for use on shipboard. Most of the other deposits of the world, except the comparatively small ones in Arizona and the recently discovered large one in British Columbia, have a substantially higher iron content, making them unsuitable for electrical insulation. Swaziland and the Republic of South Africa also produce chrysotile in substantial quantities. The Republic of South Africa produces two special types of asbestos—amosite, found commercially nowhere else, and crocidolite (blue asbestos), produced also in Australia and Bolivia. Most of the African production is exported (*24*).

Smaller operations are in Cyprus, Italy, Finland, France, Australia, Bolivia, Brazil, Japan, and several other countries.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Asbestos is a name applied to a group of naturally fibrous minerals. The principal variety is *chrysotile*, a hydrous magnesium silicate having the theoretical formula $3MgO \cdot 2SiO_2 \cdot 2H_2O$. Other commercial varieties are *amosite*, a complex iron-magnesium silicate, $(FeMg)SiO_3 \cdot 1$–5 pct. H_2O; and *crocidolite*, a sodium-iron hydrous silicate, $NaFe(SiO_3)_2 \cdot FeSiO_3 \cdot H_2O$. Of minor importance are *tremolite*, $Ca_2Mg_5Si_8O_{22}(OH)_2$, and *anthophyllite*, $(MgFe)_7Si_8O_{22}(OH)_2$ (*3*)

Chrysotile, the principal variety of commerce, is graded according to fiber length. Fibers three-eighths of an inch long or longer are classed as the spinning grades suitable for use in making fabrics. According to the Canadian classification, the crudes (hand-cobbed long fibers) and spinning fibers comprise groups 1, 2, and 3. The succeeding groups are of progressively shorter fibers. Group 4 is designated as shingle stock; group 5, paper stock; group 6, waste stucco and plaster; and group 7, refuse or shorts. Most of these groups are divided into several subgroups. Such groupings comprise the commercial specifications. The consumer designates the grade desired, such as 3R or 4K. Grades may be blended to satisfy special needs. For some uses the chemical composition is important. Thus, for electric insulation an upper limit for the iron content may be specified. The methods of classification used in the principal producing countries are discussed in detail in a Bureau of Mines publication (*4*).

TECHNOLOGY

Most chrysotile asbestos deposits, including those of Vermont and California in the United States, Canada, Southern Rhodesia, Swaziland, the Republic of South Africa, and the U.S.S.R, consist of irregular cross-fiber veins (closely packed fiber set at a right angle to the faces of the rock fractures) or slip-fiber zones (shear planes in rock filled with fiber matted together parallel to the seam) in massive serpentine. Such deposits commonly extend to unknown depths. Those of Arizona, however, consist of more or less horizontal asbestos-bearing serpentine zones in thin-bedded limestone. Such deposits are generally less extensive and less persistent than those in massive serpentine. The amosite and crocidolite of the Republic of South Africa occur in banded ironstones that

are so folded and contorted that the veins are very irregular (*16*, *24–27*).

In Vermont, the fiber-bearing rock is removed from an open pit, which is worked on three 125-foot-high benches. Similar methods are employed in the Copperopolis district in California; but in the Coalinga district the highly sheared ore is simply "plowed" and allowed to air-dry, and the coarse fraction is screened out from the millfeed. The usual practice in Arizona is to drive a 5- to 6-foot heading in barren limestone beneath the fiber zone, which is later blasted down and hand-cobbed. The Canadian mines were originally open pits, but there has been a gradual transition to underground mines using block-caving methods. The chrysotile of Southern Rhodesia, the Republic of South Africa, and Swaziland is obtained from underground mines. Amosite is obtained chiefly from large underground workings, and blue asbestos from small open pits and shallow mines. The Soviet deposits are worked both in open pits and underground. Cyprus has large open-pit workings (*5*, *17*, *21*, *24*).

Asbestos milling is a complex operation involving primarily the separation of fiber from rock and classification of the fiber by length. Asbestos, unlike the metals, is not a single commodity, but comprises a series of grades depending upon the length of individual fibers. The operator has little control over the proportions of the various grades, as they are fixed in nature, but he has the important task of minimizing fiber damage. He must mill the rock with as little fiber breakage as possible, because short fibers are worth much less than long ones. Special types of rock disintegrators have been developed, and reduction is accomplished in stages with fiber removal by air suction at each stage (*14*).

In Arizona the hand-cobbed rock is reduced in jaw crushers and the fiber separated by screening. Fiber which remains on a ½-inch screen is classed as No. 1; that which passes a ½-inch mesh and remains on a ¼-inch mesh, No. 2; through ¼-inch mesh and on ⅛-inch mesh, No. 3; and that which passes through the ⅛-inch mesh, No. 4. Nos. 1 and 2 are classed as spinning grade if the fibers are not too harsh. Some spinning fiber is obtainable from No. 3.

Special milling techniques have been developed for the matted short fiber chrysotile of the Coalinga district of California, including grinding and wet-milling processes.

In Vermont and Canada the mills are large and complex. The fiber is classified in many grades, such as spinning, cement stock, and paper stock.

USES

The uses of asbestos fibers of all varieties are numerous and range from floor tile to rockets. The longer fibers—Canadian groups 1, 2, and 3, and their equivalents from other countries—are used for making textile products such as cloth, yarn, tape, and rovings. The asbestos is spun and woven in much the same way as cotton, silk, or wool. Asbestos fabrics are used extensively for lagging cloth, brakeband linings, clutch facings, safety clothing, packings, gaskets, and various other appliances. Low-iron fiber is used in cable insulation (*2*, *13*).

Shorter fibers such as Canadian group 4, and to some extent 5 and 6, are used widely for asbestos-cement products such as roofing shingles and flat and corrugated siding. These products consist of about 80 percent portland cement and 20 percent asbestos. Canadian groups 4 and 5 and African amosite are used extensively for making 85 percent magnesia block and pipe insulation. They consist of about 85 percent basic magnesium carbonate and 15 percent asbestos. Canadian group 5 is suitable for asbestos paper and millboard manufacture. Such products are made on standard papermaking machines. An important use of asbestos paper is for making the so-called air-cell pipe covering. The shortest fibers are used for boiler and roofing cements and as filler in asphalt floor tile and various other products.

Amosite is used for felted insulation in blanket form for high-temperature service up to 900° F. A loosely compacted form is applied as a covering for marine turbines, jet engines, and similar applications. Amosite is also used as a constituent of 85 percent magnesia insulation and lightweight, fire-resistant marine partition board.

Long-fiber crocidolite (blue asbestos) is woven into fabrics used for locomotive boiler lagging (in Great Britain) and for acid-resistant packings and gaskets. The principal use of the shorter crocidolite fibers is in making asbestos-cement pipe. Bolivian crocidolite has been found useful for making gas-mask filters.

Tremolite and anthophyllite are used for chemical-resistant filters, as welding-rod coating, and as fillers in various products.

BYPRODUCTS

There are virtually no commercial byproducts at asbestos mines and mills. The fiber comprises a small part ranging commonly from 5 to 7 percent of the rock mined, and the waste rock consists of pulverized serpentine for which very little commercial use has been found. In

Vermont, however, an appreciable amount is used for road metal. The possibility of recovering magnesia from it has been proposed, but no practical method has been developed.

ALTERNATE MATERIALS

Fiberglass is used as a substitute for asbestos in some applications, chiefly in the field of heat insulation. Fabrics woven with a plied yarn having one strand each of glass and asbestos yarn are advantageous for some uses where light weight and high strength are needed. Glass filaments in submicron sizes made by highly refined processes involving the use of platinum dies are technically satisfactory substitutes for amosite in blanket insulation, but the cost is five or six times as great as that of amosite. Fiberglass is not a satisfactory substitute for asbestos in friction materials or asbestos-cement products.

Silicone products, organic compounds, and plastics are used as substitutes in certain limited applications. The use of calcium silicate, diatomite, and magnesia in some instances reduces asbestos requirements in end products.

Aluminum sheets are being used as a partial substitute for asbestos where insulation against radiant heat is required.

Synthetic asbestos has not yet been made commercially. Its current status is covered later in the section devoted to research. New types of heat-resistant plastics are being substituted for chrysotile in some forms of electrical insulation. Substantial progress has been made in substitution of Novabestos and Quinterra papers for electrical insulation. There is, however, no satisfactory complete substitute for strategic grades of chrysotile in some forms of dielectric insulation.

Fibrous glass and chrysotile asbestos are substitutes for amosite, but they are not as resistant to steam, seawater, and alkalies under all working conditions. For 85 percent magnesia and calcium silicate insulation, textile grades of chrysotile may be substituted for amosite.

Experimentation on materials that may be substituted for asbestos indicate that fiberglass can replace asbestos for some types of heat-insulating products. Cloth of good quality is made using alternate strands of fiberglass and asbestos yarn. Such substitution extends the supply of spinning-grade asbestos. Fiberglass cannot be used successfully in friction materials such as brake band linings, nor in some of the highly specialized electrical insulation uses. Recent advances in the manufacture of glass fibers offer opportunities for wider substitution. Organic plastics and silicone products have limited substitute applications.

RESERVES

In Vermont, a reserve of at least 1 million tons of chrysotile fiber appears to be assured. A small proportion of this quantity is of spinning grade. In California, measured and indicated reserves totaling more than 1 million tons are reported for the Copperopolis area; these reserves consist chiefly of types and grades similar to those in Quebec, Canada. Reserves of several hundred million tons of rock that will yield matted short-fiber chrysotile asbestos are reported for the Coalinga area in California (*20*). The Arizona reserve is difficult to estimate but is probably small.

The world appears to have an adequate asbestos reserve for at least 25 to 30 years at current or moderately enlarged rates of output. The chief suppliers of U.S. markets—Canada and the Republic of South Africa—appear to have adequate reserves for long-range planning. It is difficult to calculate South African reserves owing to the intensive folding encountered in nearly all the asbestos areas. The duplication of the asbestos bands through folding has resulted in large reserves (*18*). The U.S.S.R. reserve is probably large enough to supply its domestic economy for many years.

SOURCES OF STATISTICAL INFORMATION

Annual data on the production and shipments are obtained from domestic producers and consumption of strategic grades are reported by consumers to the Bureau of Mines.

World production and trade data also are compiled by the Bureau of Mines, and U.S. imports and exports are obtained from the U.S. Department of Commerce.

The Bureau of Mines publishes the principal statistics annually in the "Asbestos" chapter in the Minerals Yearbook.

PRODUCTION, CONSUMPTION, AND TRADE

World production of asbestos by country of origin is given in table 1. Most of the asbestos production is chrysotile asbestos, but 160,000 to 200,000 tons of the world's production each year consists of amosite and crocidolite. Table 2 shows the production of these two varieties of asbestos by country of origin.

The United States is the largest consumer of asbestos in the world. Table 3 shows U.S. asbestos consumption and imports from 1954 to 1963. Table 4 shows imports of special grades of asbestos.

From 1949 to 1953 the United States consumed on an average about 50 percent of the total world production. Domestic consumption more than doubled from 1945 to 1951, but thereafter it remained fairly constant, except for 1955, while world production continued to increase. In 1963 the United States consumed about 23 percent of the total world production.

Domestic sources furnish only a small percentage of U.S. asbestos requirements. Arizona, the only present natural source of low-iron chrysotile in the United States, has rarely produced more than 600 tons per year of the spinning grades, and the output usually has been considerably lower than that figure. A large part of the production of crudes No. 1, No. 2, and No. 3 since 1953 was purchased by the U.S. Government for stockpiling. The purchase program terminated at the end of 1962.

Vermont and the Copperopolis district of California are the only consistent U.S. producers of Quebec-type asbestos. Both are predominantly producers of short fiber, but the Vermont asbestos mines produce about 500 to 700 tons per year of spinning length fiber. Most of it is applied to nonspinning uses.

On a tonnage basis Canada furnished 90 percent of the U.S. imports (1959–63), but most of this material (97 percent) was of the shorter grades. The comparatively small quantities received from Africa are more important than would appear on a tonnage basis, because they consist largely of special kinds and qualities unobtainable elsewhere. Under emergency conditions imports of spinning fibers are of primary importance. Imports of spinning fibers from Canada average about 17,000 tons per year. The longer fibers of chrysotile suitable for spinning purposes represent a small fraction of the total production. Shortages of spinning-grade fibers have previously occurred.

The spinning grades of asbestos produced in Southern Rhodesia were of great importance during World War II and the early postwar years, because they constituted the principal source of low-iron chrysotile suitable for shipboard electric-cable construction. Production began from the new source of supply of low-iron chrysotile in northern British Columbia in 1953, and in 1962 over 5,000 tons of spinning fibers was imported from that source.

Production of amosite in the Republic of South Africa has increased from an average of 20,000 tons per year during the 1940's to 78,000 tons in 1963.

Imports of amosite into the United States from 1959 to 1963 averaged about 19,000 tons per year. Part of the imported material has been placed in the national stockpile; hence industrial consumption has been somewhat lower than the aforementioned figures. Probably

TABLE 1.—*World production of asbestos, unmanufactured, by principal countries*

[Thousand short tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963
Australia	10	18	16	17	18	15
Canada (sales)	994	1,050	1,118	1,174	1,216	1,272
China (estimate)	33	90	90	100	100	110
Cyprus	15	14	23	16	22	22
Finland	9	10	11	10	11	10
France	15	23	29	31	28	26
Italy	37	53	61	63	61	63
Japan	10	14	17	19	15	18
South Africa, Republic of	140	182	176	195	221	206
Southern Rhodesia	113	120	134	162	142	142
Swaziland	30	25	32	31	33	33
U.S.S.R. (estimate)	475	600	660	880	1,100	1,200
United States (sales)	44	45	45	53	53	67
Other countries (estimate)[1]	15	16	28	19	35	16
Total (estimate)	1,940	2,260	2,440	2,770	3,055	3,200

[1] Includes small production in about 20 countries.

TABLE 2.—*World production of amosite and crocidolite*

[Thousand short tons]

	1954–58 (average)	1959	1960	1961	1962	1963
Amosite: South Africa, Republic of	55	72	69	69	75	78
Crocidolite:						
South Africa, Republic of	62	81	78	94	116	99
Australia	8	16	14	16	17	12
Bolivia	(1)	(1)	(1)	(1)	(1)	(1)

[1] Less than 200 tons.

TABLE 3.—*U.S. consumption and imports of asbestos*

[Thousand short tons]

	1954–58 (average)	1959	1960	1961	1962	1963
Apparent consumption	729	754	709	666	726	724
Imports:						
Australia	4	9	5	2	8	(1)
Canada	637	655	617	570	624	619
Southern Rhodesia	10	5	2	3	6	4
South Africa, Republic of	32	39	41	35	35	37
Other countries	4	5	4	7	3	8
Total	687	713	669	617	676	668

[1] Less than 100 tons.

TABLE 4.—*Special grades of asbestos imported for consumption*

[Thousand short tons]

	1954–58 (average)	1959	1960	1961	1962	1963
Low-iron chrysotile (spinning lengths)	5	7	7	6	5	6
High-iron chrysotile (spinning lengths)	17	16	13	12	10	11
Amosite	14	17	20	15	20	22
Crocidolite	20	18	20	18	17	11

larger quantities would have been used had they been obtainable, because there has been and still is a stringency of supply.

Most crocidolite originates in the Republic of South Africa, but substantial tonnages are received from Australia and small quantities from Bolivia. The commercial demand for Bolivian blue is very small. African production of crocidolite has increased from an annual average of 10,000 tons during the 1940's to almost 100,000 tons in 1963. Imports of crocidolite advanced from 12,000 tons in 1954 to 18,000 tons in 1959 and dropped to 11,000 tons in 1963.

About 10,000 tons of unmanufactured asbestos was exported from the United States in 1963. The exports consist chiefly of Canadian fibers blended and prepared in various ways to suit the needs of Latin American and European buyers.

Unmanufactured asbestos enters the United States duty free.

STRATEGIC CONSIDERATIONS

Asbestos kinds and grades of greatest strategic importance are being stockpiled. The national stockpile items are spinning-grade chrysotile and amosite. Bolivian blue crocidolite is no longer considered strategic. On June 30, 1964, the maximum stockpile objective for chrysotile was 13,700 short tons. Government inventories totaled 9,287 tons, of which 6,224 was in the national (strategic) stockpile, 724 in Commodity Credit Corp. (CCC) stocks, and 2,339 tons in the supplemental stockpile. The stockpile objective for amosite was 40,000 short tons, and inventories totaled 65,838 tons, of which 11,705 was in the national (strategic) stockpile, 23,196 in CCC stocks, and 30,937 in the supplemental stockpile.

The United States is dependent upon foreign sources for 90 to 93 percent of its requirements for all grades of asbestos. The principal source of low-iron spinning grade chrysotile asbestos is British Columbia, Canada. The former chief source was Southern Rhodesia, from which our essential needs were supplied until the end of the Korean war. A small amount of low-iron long-fiber chrysotile is available from Arizona. The only source of commercial grades and quantities of amosite is a limited area in Transvaal, Republic of South Africa. The United States is also completely dependent on foreign sources for crocidolite.

GOVERNMENT PROGRAMS

During World War II controls were in effect to restrict exports of asbestos needed in the military program. These controls were removed by executive order on September 10, 1945. During the Korean war the supply situation again became acute, and in 1950 and 1951 controls were invoked that required licenses for export of all grades of asbestos. The license requirement was removed for the nonspinning grades in 1953, and for the spinning fibers in 1954; however, export licenses are required for shipments to Communist nations.

The allocation of asbestos supplies effected during World War II has been deemed unnecessary since the Korean war, but the National Production Authority (NPA) issued an order (M–96 dated January 17, 1952) that gave priority to military and essential civilian uses of the limited supply of spinning grades of chrysotile asbestos. It prohibited the use of certain grades of spinning fiber for other than certain specified end uses. As supplies of spinning-grade chrysotile had become adequate for all commercial and military needs early in 1953, order M–96 was revoked by the NPA May 12, 1953.

The discovery and development of new asbestos deposits have always been a most urgent necessity. To assist in discoveries the Office of Minerals Exploration (OME), and the Defense Minerals Exploration Administration which was abolished in 1958 and whose functions were assumed by OME approved 19 asbestos exploration contracts as of December 1963. Only five contracts led to certification of discovery and none of these were significant to the overall supply situation.

A government depot in Globe, Ariz., was opened for the purchase of domestically produced asbestos meeting certain specifications. Under Public Law 733 (1956), a government purchase program at premium prices for domestic low-iron chrysotile asbestos was established which was terminated on December 31, 1958. In 1959 the stockpile objectives for low-iron chrysotile were raised, and a barter program was established to acquire the additional fiber needed through exchange of agricultural surpluses. The U.S. Department of the Interior recommended purchase of 500 tons of low-iron chrysotile from domestic mines to assist the domestic industry and to establish a domestic mobilization base for production.

Amosite and chrysotile have been acquired for the stockpile by purchase and barter, and crocidolite has been acquired by barter.

PRICES

Although asbestos has had an erratic price history, prices during the past 5 years have remained relatively stable. Quebec chrysotile fiber prices in 1963, f.o.b. mine, ranged from Can$40 per short ton for 7T, which is the short-

est of the regular fiber grades generally produced, to Can$875 for the longest of the milled fibers. Crude No. 1 sold for Can$1,410 or more per ton. British Columbia fibers sold from Can$142 for AX to Can$1,522 per ton for crude No. 1.

Vermont chrysotile is produced in grades similar to those of Canada and ranged in price in 1963 from $40 for group 7 to $402 for group 3, f.o.b. mine. Arizona fibers ranged in price from $58 for group 7 to $1,650 for crude 1, f.o.b. Globe, Ariz. (*1*).

As sales of African and Australian asbestos are negotiated separately, market quotations are not available.

TAXES

There are no special taxes on the asbestos industry. Producers are granted a depletion allowance of 23 percent on domestic production and 10 percent on foreign production.

TRANSPORTATION

The Quebec and Vermont deposits are within easy rail haul to most of the plants manufacturing asbestos products in the industrial areas of the Eastern United States. The African deposits are remote from the principal markets and have high transportation expenses. Transportation from British Columbia is difficult and costly, but a shorter route is in prospect. The Arizona miners have difficult transportation problems. The mines are in the vicinity of Globe, the nearest railhead, at distances ranging from a few miles to 104 miles, with an average haul to the railroad of about 50 miles. The major consumption centers are in the Northeastern United States, and are much closer to Quebec, Canada, than to Arizona. Consumption of asbestos is growing along the west coast of the United States. Comparable growth of the industry has taken place in other areas where fiber from California would be competitive, in terms of freight rates, with that from Quebec.

RESEARCH

Research on production has been conducted by companies operating mines in Canada. Substantial research has been conducted on utilization of the more plentiful shorter grades in applications where longer grades are preferred. For instance, it has been found that more complete fiberization, permitting better contact of cement and fiber, will allow groups 5 and 6 to be blended in increasing proportions with group 4 in making asbestos-cement products.

Two companies have developed processes for reducing the iron content of Quebec asbestos to make it suitable for electrical uses. The Johns-Manville Corp. manufactures Quinterra paper from such fibers. Raybestos-Manhattan, Inc., has developed a process for making a low-iron product known as Novabestos. Both Quinterra and Novabestos papers may be interlaminated with a fiberglass fabric or grid to give additional strength. These products are now manufactured commercially and are used extensively in cable construction and for other nonferrous applications.

The Cape Asbestos Company Ltd., London, has investigated tensile testing of crocidolite and amosite, their chemical resistance, and their behavior in solutions of various chemicals and surface active agents. The only laboratory in the world devoted entirely to fundamental research on asbestos fibers was recently constructed by Turner and Newall Ltd., Manchester, England. New types of equipment were developed to sort asbestos fibers according to diameter and length (*19*).

In this country, the Naval Research Laboratory has conducted experimental work on the possible use of a papermaker's Vortrap to remove iron minerals from Canadian chrysotile. The Bureau of Mines conducted similar experimental work with its own equipment. The tests indicated that the magnetic iron content of ordinary Quebec asbestos can be reduced to satisfy the requirements of 2 percent or less stipulated in the national stockpile specification for nonferrous chrysotile.

The Naval Research Laboratory has developed a fiberglass gas mask filter said to be superior to those made of Bolivian blue asbestos. Bolivian crocidolite is, therefore, no longer regarded as essential.

Much work has been done on the synthesis of asbestos, but limited progress has been made. The Bureau has synthesized amphibole asbestos, but the fibers made are weak and brittle. The Bureau also has synthesized asbestiform compounds not found in nature that have some of the properties of asbestos. Chrysotile, the type of asbestos most in demand, is difficult to synthesize. Fibers of submicroscopic length only have been made (*9–12*, *15*, *22–23*). The Bureau has performed core drill tests on various properties to determine the occurrence of asbestos, and the Geological Survey has studied the geology of asbestos deposits in various parts of the country (*6–8*, *16*, *25–27*).

OUTLOOK

The trends in the consumption of asbestos will follow those of industrial production and building construction. Asbestos will continue to find wide industrial use in friction materials, pipe insulation, packings, gaskets, plastics, and many other products. Also, large quantities of asbestos will be used for asbestos-cement pipe, roofing and siding products, floor tile, insulation, moulding compounds, and millboards. The demand in the United States for all types and grades of asbestos should increase 3 to 5 percent annually. Annual consumption of asbestos should reach 900,000 tons in 1965–70, and may exceed 1 million tons by 1975 in the absence of an industrial recession. Domestic production should increase annually and attain 95,000 tons per year during 1965–70; consequently, domestic mines will supply 10 percent of the Nation's overall requirements. Most of the supply, however, will consist of nonspinning, low-unit-value fiber.

As new markets come into being and old markets grow, world production of asbestos fibers will rise. As worldwide demand for asbestos increases, there is much interest in exploring new areas. New occurrences in Ireland, Australia, and Mexico have been examined. Additional mills in Quebec, and others in prospect, assure rising availability of supplies. Newly discovered deposits undergoing exploration and development, in northern Newfoundland, Quebec, Ontario, and British Columbia, promise further expansion and output. Expansions have also taken place in the U.S.S.R., Southern Rhodesia, and the Republic of South Africa where all types of asbestos are produced. Utilization of short-fiber grades is growing throughout the world. Deposits rich in short-fiber chrysotile, being developed in California, will add substantially to domestic production as markets are found. No spinning-grade fiber is expected from these deposits. Imports are expected to increase from Canada, Southern Rhodesia, and the Republic of South Africa. Supplies of asbestos apparently will be adequate for both short-term (5-year) and long-term (10-year) requirements. World production has doubled over the past 10 years to the present 3.2 million tons. World demand is expected to require world output of 4 to 5 million tons within the next decade.

U.S. requirements for low-iron chrysotile of spinning-grade quality have been greatly reduced because of the decline in military usage and the substitution of other electrical insulation materials, such as fibrous glass, plastics, and silicone rubber. Some Quebec fibers are now processed in such a manner that their iron content is reduced sufficiently to make them suitable for some electrical insulation. However, the United States still needs about 2,500 tons per year of low-iron fiber. Beneficiated chrysotile imported from Quebec is being used in the manufacture of low-iron fibers. Imports of low-iron chrysotile from British Columbia will be adequate to meet special needs and provide a surplus for general-purpose uses. Low-iron tapes and papers using beneficiated chrysotile imported from Quebec are suitable for some electrical insulation, thereby relieving part of the demand for low-iron fibers. Arizona mines will remain a small factor in industrial supply.

High-iron spinning-grade chrysotile requirements for the short-term are estimated at almost 20,000 tons per year, increasing over a 10-year period to 25,000 tons. Most of the supply comes from Canada, with small amounts produced in Vermont and imported from Africa and other overseas sources. Information from the Canadian Department of Mines and Technical Surveys indicate that Canadian production of spinning grades is about 30,000 tons per year. The industry could produce about double this quanitity if the market so required. Approximately 50 percent of the supply is currently exported to the United States. From this it appears that Canada is an adequate source for all foreseeable requirements.

Amosite requirements of the United States are increasing steadily. Imports reached nearly 22,000 tons in 1963 and will probably increase to 30,000 tons per year within the next 10 years. Mining and milling facilities are being expanded in the Republic of South Africa and are expected to remain above the short-term and long-term requirements. Amosite is particularly suitable for use in heat-insulating materials.

Crocidolite requirements have increased substantially during the past 5 years. The long-fiber grades are in relatively small demand, but use of the shorter fibers in asbestos-cement pipe manufacture is increasing rapidly. With expanding facilities for pipe manufacture in the United States, demand for crocidolite may reach 30,000 tons per year within 10 years. Large deposits of crocidolite are known only in the Republic of South Africa and Australia. African production facilities are being expanded as new fiber-bearing zones are discovered and developed. Production of crocidolite in Australia increased 30 percent during 1958–62. Reserves are said to be extensive.

The outlook for successful synthesis of commercial asbestos remains uncertain.

PROBLEMS

The complete dependence of the United States on foreign sources for some types of asbestos is an important problem that concerns the national economy and defense needs. Export duties and other controls by producing countries could increase costs to U.S. consumers.

The disposal of surplus inventories of asbestos in the Government stockpiles is of concern to the producing industry. The absence of any clearly defined and predictable long-term disposal program has heightened this concern.

More data are needed on the fundamental characteristics of asbestos to serve both as a foundation for future research on synthesis and as a guide to new and improved usage of all varieties of fiber.

Information is needed on the interchangeability of the many types of asbestos in manufactured products. Development of substitutes for scarce types and grades or asbestos fiber is a difficult problem because of the superiority of asbestos to other materials for special use.

The biological effects of asbestos are a serious health problem in the industry. The hazards are recognized, however, and adequate filtering and ventilation are provided in processing plants. The extensive use of asbestos in a variety of industrial applications has drawn attention to the medical problems associated with this use. These problems include pulmonary asbestosis and neoplasia associated with occupational exposure to asbestos.

Other problems include occasional shortages of spinning-grade fiber, utilization of waste from asbestos plants, and the development of potential large-scale uses for the widespread resources of actinolite, anthophyllite, and tremolite varieties that are in little demand.

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BARIUM

By Richard W. Lewis [1]

TWO barium minerals, barite ($BaSO_4$) and witherite ($BaCO_3$) serve a wide variety of markets. Chemical inertness, high density and low cost make barite especially suitable for well-drilling muds, which is by far its greatest use. Witherite is of minor commercial importance to the barium chemical industry. Furthermore world supplies of witherite are quite limited whereas ample barite reserves are dispersed throughout the world.

Domestic production of barite totaled 803,000 short tons in 1963. There was no domestic production of witherite, the other commercial barium mineral, in 1963, but some was imported. Twelve States reported production of barite in 1963. Arkansas and Missouri—the leading barite-producing States—along with Georgia and Nevada accounted for 92 percent of the total. Barite is mined by both open-pit and underground methods and at some operations is concentrated by flotation.

Consumption remained at about the same level from 1958 through 1963 except that in 1959 it was about 200,000 tons higher owing to increased demand for oil-drilling mud. No appreciable change from this is expected during the next 4 or 5 years.

Domestic measured and indicated reserves of barite are estimated to total about 46 million tons; the largest reserves are in Missouri, Arkansas, Nevada, and California. The inferred barite reserve is estimated at 67 million tons.

The problems of heavy dependence on a single market, of locating additional deposits near major consuming areas, and of maintaining a satisfactory reserve position are of long-range importance to the industry. Research is needed on methods of exploring for new deposits and on the recovery of barite from complex ores and waste products. In addition, research on the properties of barium compounds and for new uses is required.

BACKGROUND

The domestic barite industry dates back to the middle of the 19th century when, in 1845, production of barite was first reported in Fauquier County, Va. About 5 years later, production was begun in Missouri. In 1880 Tennessee became the third barite-producing State; and 1901 and 1903 saw Georgia and Kentucky, respectively, become producers. California came into production in 1914, and in 1941 the deposit of barite at Malvern, Ark., was opened when Magnet Cove Barium Corp. successfully separated barite from associated minerals by flotation. The first washers and jigs used in the industry were installed in Georgia and Tennessee in 1914–16 and in Missouri in 1923–24.

Barite's first use was as a filler in white paints; however, in 1892, with the advent of the domestic lithopone industry, a second important market was opened. In 1908 Chicago Copper Refining Co. (now Chicago Copper & Chemical Co.) began manufacturing barium chemicals at Blue Island, Ill. A fourth market for barite came into existence in 1926 when a patent was obtained on the use of barite as a weighting agent in rotary drilling muds. This today is the largest use of barite.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

The two principal producers of barite in the United States are Baroid Sales Division, National Lead Co., and Magnet Cove Barium Corp., a subsidiary of Dresser Industries. In addition several firms produce 40,000 to 100,000 tons annually, and numerous smaller firms produce less than 40,000 tons annually. The

[1] Commodity specialist.

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smaller firms usually sell their production to the large producers or to custom grinders. A total of 41 firms produced crude barite in 1963.

There were 13 producers of barium chemicals and 2 producers of lithopone in 1963. Of these, only one firm owns its source of raw material.

The two leading barite-producing States are Arkansas and Missouri; Georgia and Nevada are also major producing States, while California, Idaho, Kentucky, New Mexico, Montana, South Carolina, Tennessee, and Texas recorded minor production in 1963. Occasionally output has been reported from Arizona, Utah, and Washington.

Most of the barite produced in California and Nevada is consumed by oil and gas well drillers and the barium chemical industry in California. Output from Montana and Idaho is used in oil exploration in those and nearby States, and some is exported to Canada. Virtually all of the Arkansas and most of the Missouri production goes to midcontinent and gulf coast well drillers. The remainder of Missouri's production is consumed by the paint, glass, and chemical industries in the Midwestern and Eastern States. Oil well drillers in Texas and Louisiana are supplied partially from Southeastern production and from Texas with the remainder imported.

Barite occurrences have been recorded on every continent and in every major country. Some domestic producers have interests in deposits in Brazil, Greece, Mexico, and Canada.

Some of the more important barite-producing countries other than the United States are Canada, West Germany, Italy, Mexico, Morocco, the U.S.S.R., and Yugoslavia. Output has been reported from at least 35 countries.

The only commercial production of witherite is in Northumberland, England, from where it is exported to consuming countries. Some witherite was produced prior to 1948 in Mariposa County, Calif.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Two minerals are commercial sources of barium and barium compounds. They are *barite* ($BaSO_4$), the principal mineral of commerce, and witherite ($BaCO_3$). Barite theoretically contains 65.7 percent barium monoxide (BaO) and 34.3 sulfur trioxide (SO_3) and has a specific gravity of 4.5; witherite contains 77 percent BaO and 22.3 percent carbon dioxide (CO_2). Its specific gravity is 4.3. A high specific gravity gives barite its major use as a weighting agent in drilling muds.

The term "barite," the correct mineralogic name, is derived from the Greek word "barys," meaning heavy. The mineral of commerce is commonly referre dto as "barytes," locally in Missouri as "tiff," and in various other localities as "heavy spar."

Specifications for barite vary with its different uses.

Drillers require the material for oil well-drilling muds to be fine-ground, heavy, and chemically inert; consequently, barite for this purpose must contain a minimum of 92 percent $BaSO_4$, be free of soluble salts, and have a minimum specific gravity of 4.2; 90 to 95 percent of the material must pass a 325-mesh screen. Several percent iron oxide is not objectionable.

Barite for chemical manufacturing must meet more stringent specifications. A minimum of 94 percent $BaSO_4$ and a maximum of 1 percent each for ferrous oxide (Fe_2O_3) and strontium sulfate ($SrSO_4$) and only a trace of fluorine are usually specified. If the material is to be used for lithopone, the $SrSO_4$ content may be somewhat higher. Mesh size is important to chemical producers; if material is too fine dust is lost, and if it is too coarse mixing with carbonaceous material is poor. A size specification range of 4- to 20-mesh is requested by most consumers; however, some purchase lump barite and grind it to this specification.

Glass manufacturers usually require a minimum of 98 percent $BaSO_4$ and a maximum of 1.5 silicon dioxide (SiO_2), 0.15 aluminum oxide (Al_2O_3), and 0.15 Fe_2O_3. In mesh size a mixture ranging from 30-mesh down through 140-mesh is preferred. Material ground to 325-mesh is not desired because it tends to ball up in the batch, but it has been used in times of short supply. Iron is the most objectionable impurity.

Specifications for barite used as a filler or in aggregates are less strict; in most instances mesh size is most important.

TECHNOLOGY

Geology

Most commercial barite deposits are of two types: Replacement deposits, either total or partial, of limestones, dolomites, sandstones, and shales; and residual deposits in which lumps of barite, weathered from deposits of type 1, are enclosed in clays. Barite also occurs as a gangue mineral or associated mineral in metalliferous ores such as lead, zinc, and silver and in mixtures of fluorspar and barite in Kentucky, New Mexico, and elsewhere.

The Arkansas, Nevada, and California deposits are examples of the replacement type.

At Magnet Cove, Ark., barite occurs in a shale. Chert, flint, pyrite, various carbonate minerals, and iron oxides occur dispersed throughout the barite horizon.

Residual deposits include those occurring in Missouri, Tennessee, Georgia, and other Eastern States.

In South Carolina, barite occurs as fissure veins and lenses in a quartz sericite schist and has also been reported occurring disseminated throughout the schist.

Detailed descriptions of various barite deposits are given in the publications listed in the bibliography.

Mining and Milling

The methods of mining and preparing barite depend on the type of deposit and the ultimate use. Residual barite deposits are mined by open pit methods. The clay is removed in log washers, and fine barite contained in the overflow may be recovered by tabling and froth flotation. Barite mined in Arkansas is recovered by both open pit and underground methods. The material is ground and beneficiated by froth flotation. In some locations, barite occurring in veins is mined by shrinkage stoping methods and recovered by jigging.

Barite is ground either wet or dry depending on whether it is to be bleached. For use in well drilling or filler, it is ground dry in ball or Raymond mills. Arkansas material, since it must be floated, is wet-ground. In Georgia, barite is dry-ground in a roll mill. In Missouri, unbleached barite is dry-ground and material to be bleached is wet-ground. Details of the bleaching operations are considered trade secrets, but the general principles are well known. The impurities are brought into solution by treating the ground barite with sulfuric acid; the pulp is then settled and separated and the impurities are washed out. This is followed by drying and packing.

Before being converted to lithopone or barium chemicals, barite is converted into an intermediate soluble form. This is accomplished by roasting crushed barite in a kiln with carbon to reduce barium sulfate to the more soluble barium sulfide, commonly called black ash. The black ash is leached with hot water. To make lithopone, a solution of zinc sulfate is added to the leach liquor and an intimate mixture of barium sulfate and zinc sulfide is produced. This mixture is then filtered, washed, and dried. Blanc fixe is made by adding sodium sulfate to the black ash solution and precipitating barium sulfate. Barium carbonate is manufactured by adding sodium carbonate to the black ash solution and precipitating barium carbonate. Barium carbonate is the starting point for manufacturing various other barium chemicals.

USES

The most important use of barite is as a weighting agent in well-drilling muds. Drilling muds serve several purposes; they lubricate and cool the bit, plaster the walls of the drill hole to prevent caving, carry the cuttings up the well to the surface, and (the purpose for which the barite is used) restrain high gas and oil pressures to their formation levels to prevent blowouts. This type of drilling mud was patented in 1926 and placed on the market under the trade name "Baroid" by National Pigments and Chemical Co. (now National Lead Co.). A royalty of $13 per ton was charged until the patent expired in 1943.

Crushed barite (16- to 20-mesh) is used by the glass industry. This material when added to the glass melt fluxes the heat-insulating froth that forms on the surface of the melt, thus saving fuel, and also acts as an oxidizer and decolorizer, making the glass more workable and increasing brilliance. Fine-ground barite can be used for this purpose when crushed material is not available.

Barite is also used as a filler or extender in paint, inks, oilcloth, linoleum, rubber, and other materials.

Barite is the raw material used in manufacturing lithopone which is used as a white pigment in paints, and various barium chemicals such as barium carbonate, precipitated barium sulfate, barium chloride, barium oxide, barium peroxide, barium hydroxide, barium nitrate, and others.

Blanc fixe, precipitated barium sulfate, is used as a white filler in paints, rubber, inks, and other material where a higher degree of purity is required than is found in the natural barite.

Barium chloride is used in case hardening, in leather and cloth, in making magnesium metal, in preventing scum on brick, and in water treatment. Fused barium chloride may be electrolyzed to produce barium metal.

Barium carbonate is used as a component in ceramic glazes and enamels and also to prevent formation of scum on ceramics. It diminishes porosity and prevents discoloration in bricks and is used in making crown and flint glasses.

Barium oxide is used in glass and in manufacturing barium peroxide. In electric ferrous metallurgy it is used to increase the life of acid furnace linings, give a quieter and steadier arc, and reduce sulfur and slag viscosity.

Barium hydroxide prevents scumming in ceramics and is used in lubricating oils and to

recover sugar from molasses by the barium saccharate process.

Barium nitrate is used in green signal flares, in primers or detonators, and in enamel.

Barium metal is a deoxidizer of copper. It is used as a getter to remove last traces of gas from vacuum tubes, and because of its high electron emission rate when subjected to an electrical potential, it is used in alloys for spark plugs and electron emission elements in electronic tubes.

Barium titanate has become extremely important to the electronic industry because of its high dielectric constant and its piezoelectric and ferroelectric properties. The compound is exceptionally suitable for use in miniature electronic and communication equipment.

Finely-ground barite is mixed with synthetic rubber powder and added to asphalt for road, airstrip and parking lot construction. Advantages claimed by this surfacing material are a more flexible seal coat and less cracking of the surface, thereby giving longer life to the road surface.

Witherite, the natural barium carbonate, is used in refining sugar, manufacturing of barium chemicals, case hardening, and pigments.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Some barite has been produced as a byproduct from a lead operation in New Mexico. Barite is frequently associated with fluorspar, but no commercial separation plants are in operation in the United States. However, some barite-fluorite mixtures are used in the glass industry.

Barite, satisfactory for use as a filler in paint manufacture, is separated as a byproduct from the production of acid-grade fluorspar in England.

ALTERNATE MATERIALS

In its largest use, as a weighting agent in drilling muds, barite is preferred to other materials because it is clean to handle, relatively inexpensive, nonabrasive, inert, and has a relatively high specific gravity. During 1926–43, when a royalty was charged on the use of barite in drilling muds, celestite, although having a lower specific gravity (3.95–3.97), was used. It does not now compete in this field. Some iron ores are heavier and in about the same price range as barite; there seem to be no technical reasons why they cannot be substituted, except that they are slightly more abrasive and soil personnel and equipment. Galena, with a specific gravity of 7.4 to 7.6, is much more expensive and has some technical disadvantages. Although substitution appears possible, the use of ground barite in this application is expected to maintain its position.

Lithopone has competition in the pigment field from titanium dioxide. The latter, although about 1 cent per pound higher in price, has largely replaced lithopone.

RESERVES

The domestic commercial reserve of barite ore was estimated by the Geological Survey in 1958 to be about 285 million tons of measured and indicated ore, containing about 46 million tons of barite. The inferred reserve totals more than 365 million tons of ore, containing about 67 million tons of barite. The reserves are principally in Missouri and the southern Appalachian States; the remainder is in Arkansas, Nevada, and California (*2*).[2]

The reserve of chemical-grade barite, because of the strict chemical and physical specifications, is more limited than that of other grades, but requirements can be satisfied with beneficiated ore.

Complete information on foreign reserves is lacking. The Nova Scotian reserve has been estimated in excess of 3 million tons, and that in the region of Camamu Bay, Brazil, in excess of 800,000 tons.

CONSERVATION PRACTICES

Many firms have improved mining methods and initiated flotation processes for the recovery of barite fines previously lost in washer operations. Barite is seldom if ever recovered as a byproduct of metal-mining operations when it occurs as gangue or an associated mineral. There are no estimates of the quantity that has been discarded to dumps or of the present rate at which it is being discarded. A substantial portion of this barite could be recovered if an economical process was available.

In most uses, barite is consumed or incorporated into the product and is not recoverable, the one exception being the material used in drilling muds. In this use some of the barite is lost, but most of it is returned to mud ponds on the surface. Recovery of barite from the mud pond for reuse on deep wells is fairly common practice. However, upon completion of the well, usually the barite in the pond is abandoned.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

SOURCES OF STATISTICAL INFORMATION

The Bureau of Mines annually canvasses the producers of crude barite, ground barite, barium chemicals, and lithopone. Data collected on the crude barite use pattern include quantities used in making crushed and ground barite and in the chemical industry. The Bureau also publishes data on world production. Imports for consumption and exports are compiled from official statistics of the U.S. Department of Commerce.

PRODUCTION, CONSUMPTION, AND TRADE

Domestic production of barite was a record 1,352,000 short tons in 1956 but dropped to a very low 486,000 tons in 1958. Many mines that were inactive in 1958 resumed operations in 1959, increasing production of primary barite to 867,000 tons. During the past 3 years (1961–63), domestic output has remained rather stable with a variation from the mean of less than 10 percent (table 1). Table 2 shows the amount of domestic barite sold or used by producers.

Production of lithopone in the United States has declined. In 1947 there were eight operating plants with sales totaling 165,024 tons valued at more than $17.3 million. Sales dropped to 38,000 tons in 1956 from four operating plants, and by 1958 two more plants were phased out. In 1963 only one firm produced lithopone.

Consumption of ground barite in its major use, drilling mud, increased to a high of 1,421,033 tons in 1956 and then declined slowly to 907,134 tons in 1963. However, there has been some increased use in other industries for ground barite (table 3). Table 4 shows the amount of crude barite used in the manufacture of ground barite and barium chemicals.

Imports have averaged about 640,000 tons for the past 3-year period (1961–63) (table 5). Most of the imported barite is brought into Texas and Louisiana where it is processed in grinding plants for use in well drilling while smaller quantities are delivered to east coast ports for use in the chemical and glass industries.

Crude or otherwise unmanufactured barite is dutiable at $2.55 per long ton. Ground or otherwise manufactured barite has a tariff of $6.50 per long ton levied upon it. Crude witherite is imported duty free, whereas ground witherite has a duty of 12.5 percent ad valorem.

The tariff on barium chemicals varies with each compound. The duties on selected barium chemicals follow:

	Cents per pound
Barium carbonate, precipitated	1.2
Barium chloride	1.6
Barium dioxide	4.8
Barium hydroxide	1.25
Barium nitrate	1.0
Barium oxide	2.0
Barium sulfate, precipitated (blanc fixe)	.625

Other barium compounds are dutiable at 10 percent ad valorem.

TABLE 1.—*Domestic production of primary barite*

[Thousand short tons]

Year	Production	Year	Production
1954–58 (average)	1,037	1961	731
1959	867	1962	887
1960	771	1963	803

TABLE 2.—*Domestic barite sold or used by producers in the United States, by States*

[Thousand short tons and thousand dollars]

State	1961		1962		1963	
	Quantity	Value	Quantity	Value	Quantity	Value
Arkansas	278	$2,630	259	$2,232	236	$2,161
California	21	295	7	133	5	76
Georgia	107	2,046	109	1,987	117	2,013
Kentucky	(1)	(1)	(1)	(1)	6	85
Missouri	227	3,052	304	3,994	287	3,680
Nevada	130	863	138	954	120	760
New Mexico	(1)	(1)	(1)	(1)	1	6
South Carolina	13	253	16	327	(1)	(1)
Tennessee					24	404
Other States [2]	21	161	27	193	28	262
Total	797	9,300	860	9,820	824	9,447

[1] Included with "Other States" to avoid disclosing individual company confidential data.
[2] Kentucky (1961–62), New Mexico (1961–62), Idaho (1961–63), Montana (1961–63), Texas (1961–63) and South Carolina (1963).

TABLE 3.—*Ground and crushed barite sold by producers, by consuming industries*

Industry	Short tons	Percent of total	Short tons	Percent of total	Short tons	Percent of total
	1954–58 (average)		1959		1960	
Well drilling	1,180,284	94	1,153,560	95	920,283	94
Glass	24,418	2	12,165	1	15,012	1
Paint	19,811	1	17,046	1	18,273	2
Rubber	21,475	2	19,806	2	17,082	2
Undistributed	7,364	1	7,330	1	6,180	1
Total	1,253,352	100	1,209,907	100	976,830	100
	1961		1962		1963	
Well drilling	941,539	91	934,007	91	907,134	89
Glass	30,713	3	39,017	4	56,362	5
Paint	16,128	2	19,786	2	34,611	3
Rubber	24,007	2	26,235	3	28,479	3
Undistributed	23,395	2	4,045		3,121	
Total	1,035,782	100	1,023,090	100	1,029,707	100

TABLE 4.—*Crude barite (domestic and imported) used in the manufacture of ground barite and barium chemicals in the United States* [1]

[Thousand short tons]

Year	In manufacture of—		Total
	Ground barite [2]	Barium chemicals and lithopone	
1954–58 (average)	1,339	176	1,515
1959	1,227	170	1,396
1960	1,005	185	1,190
1961	1,224	167	1,391
1962	1,043	167	1,210
1963	1,048	152	1,200

[1] Includes some witherite in the manufacture of barium chemicals.
[2] Includes some crushed barite.

TABLE 5.—*U.S. imports for consumption of barite, by countries*

[Bureau of the Census]

Country	1961		1962		1963	
	Short tons	Value	Short tons	Value	Short tons	Value
Crude barite:						
Brazil	19,351	$150,490	10,685	$87,240	13,070	$94,856
Canada	145,043	1,232,892	221,070	1,883,119	150,881	1,187,460
Greece	63,926	415,219	34,328	260,525	48,081	362,454
Ireland					10,483	70,200
Italy	7,276	90,940	5,268	72,028		
Mexico	133,733	1,076,905	243,138	1,716,263	159,964	1,081,821
Morocco	58,240	528,989	44,934	418,402	51,784	430,028
Peru	109,986	1,039,056	105,560	978,809	91,295	903,158
Spain	10,204	112,542	18,726	167,330	18,852	183,829
Yugoslavia	60,401	537,714	53,019	424,564	33,688	323,571
Total	608,160	5,184,747	736,728	[1] 6,008,680	578,098	4,637,377
Ground barite:						
Canada	6,935	503,262	18	690	13	375
Germany, West	33	1,653	32	1,401	23	896
Mexico			89	890	243	3,890
Spain					17	450
Total	6,968	504,915	139	2,981	296	5,611

[1] Includes barite imported from the United Kingrom valued at $400.

STRATEGIC CONSIDERATION AND GOVERNMENT PROGRAMS

Barite and barium compounds are not on the list of strategic and critical materials to be acquired for the national stockpile. The industry is widely dispersed throughout the Nation; the major concentration is in the center of the country. The United States is potentially self-sufficient; the major problem is mine and plant capacities.

Transportation of imported material during wartime would present a problem; however, since the two major sources of imports are Nova Scotia and Mexico, this problem would be minimized.

On August 1, 1952, the Defense Production Administration set an expansion goal for barite of an annual capacity of 1,360,000 tons by 1955 to meet the needs of the defense program. This program was closed August 11, 1955. No new programs have been initiated since.

PRICES

Barite prices increased steadily from about 1948 to 1958 but have changed little during the last 5 years (1959–63). In 1948 crude barite was priced at about $9 to $10 per short ton; ground well-drilling grade averaged about $17 per ton; and water-ground, bleached barite, in bags, about $35 per ton. In 1958 corresponding prices were $16 to $18 per ton for crude, $26.75 per ton for the ground well-drilling grade, and $45 to $49 for the water-ground bleached material.

The current market prices on barite as quoted in E&MJ Metal and Mineral Markets are as follows (unless otherwise stated, prices are for short tons, f.o.b. shipping point, in carload lots):

Chemical grade:	
Hand picked, 95 percent $BaSO_4$, 1 percent iron	$18.50
Beneficiated, 96 to 97.5 percent $BaSO_4$, 0.3 to 0.7 percent iron	$19.00–23.50
Water ground, 99.5 percent $BaSO_4$, 325-mesh, in 50-pound bags	45.00–49.00
Drilling-mud grade, 83 to 93 percent $BaSO_4$, 3 to 12 percent iron, 4.20 to 4.30 specific gravity:	
Crude	12.00–16.00
Some restricted sales	11.50
Ground	26.75
Imported, bulk, c.i.f. gulf ports	11.00–14.00
Canada:	
Crude, bulk, long tons, f.o.b. shipping point	11.00
Ground, 100-pound bags, short tons, f.o.b. shipping point	16.50

Prices of barium chemicals and lithopone are quoted in the weekly editions of Oil, Paint and Drug Reporter. An annual summary of the prices is published in the commodity chapter of the Bureau's Minerals Yearbook.

Prices of some selected barium chemicals in 1963 were as follows: Barium carbonate, precipitated, bags, carlots, works, short ton $111.50; barium chloride, anhydrous, bags, carlots, works, short ton $176; barium hydrate, crystalline, bags, carlots, truckloads, delivered, short ton $208 to $224; barium nitrate, barrels, carlots, truckloads, delivered, pound $0.16; barium oxide, ground, drums, carlots, truckloads, delivered, short ton $275 to $288; blanc fixe, direct process, bags, carlots, works, short ton $160.

TAXES

Federal tax laws allow barite producers a percentage depletion allowance both domestic and foreign of 15 percent of gross income, not to exceed 50 percent of net income without the depletion deduction. Some producing States levy severance taxes.

TRANSPORTATION

Transportation is an important factor for a relatively low-priced commodity such as barite. It is the low cost of water transportation that permits Nova Scotia barite and other foreign deposits close to water transportation to compete successfully with domestic material on the Atlantic and gulf coasts.

Barite is shipped in bulk and in bags by water, truck, and rail. Some ground material is packed in 100-pound bags and shipped in boxcars to distributors, and some is shipped in bulk in covered hopper cars to oilfield destinations from which it is transported to the wells in specially built trucks.

Crude barite is shipped in bulk, usually in open gondola cars.

Self-maneuvering barges are used for delivering barite and other drilling-mud components to offshore drilling rigs. Material can be transported either in bulk or in bag form; if in bulk it is transferred to the rig pneumatically by hoses, and if in bags by hoists.

RESEARCH

Barite deposits in Arizona, Arkansas, Kentucky, New Mexico, North Carolina, and Tennessee have been investigated and described by the Bureau of Mines (*4*, *7*, *13*, *17*, *18*, *23*, *27*).

Active exploration for new deposits near major consuming centers is underway both here and abroad by industry.

The Bureau has conducted research on processes for separating barite from fluorite and other constituents of complex ores. Continuous flotation tests yielded a barite concentrate containing 91.2 percent $BaSO_4$ with an 85.2 percent recovery. A good grade of fluorspar also was recovered (*8*). Other research by the Bureau included investigation of barite ore treatment methods and processes for making barium and its alloys (*9, 10, 15, 21*). Industry also has been active in barite recovery processes.

Other flotation processes have been reported for the recovery of the barite from ores and drilling fluids (*1, 12, 16, 25*).

Research continues on production, properties, and applications of barium titanate ceramics. The interest in this compound has been created by its dielectric and piezoelectric properties. Barium ferrite ceramics also are being carefully studied. Useful single crystals were grown and their microwave properties were determined.

Research on many other compounds containing barium should ultimately lead to new uses.

OUTLOOK

The barite industry will continue to depend on oil and gas well drilling as the major consuming industry. A current surplus of domestic and foreign petroleum production capacity coupled with rising exploration costs is acting as a brake on new oil exploration activity, which in turn has caused barite consumption to decline. Annual consumption by this industry has fallen from a peak of nearly 1.5 million tons in 1957 to an average of about 0.9 million tons in 1960–63. This production level will probably be held until there is an increase in exploration activity by the petroleum industry.

The decline in barite consumption by its major consumer has been masked by sharp rises in consumption by the paint, glass, and rubber industries. The rise in use by paint and glass manufacturers has been exceptionally sharp, reversing a long-term decline, while use by the rubber industry has risen sharply and continues a long-term upward trend. It is doubtful that the steep rises will be sustained over a long period; the overall outlook is for stabilized or declining consumption.

Imports should capture more and more of the domestic market, especially if tariffs are reduced.

The replacement of lithopone by titanium dioxide as a white pigment should continue, and requirements for barite in this field have been reduced considerably.

If construction of nuclear reactors increased, barite might find greater use as an aggregate in the production of high-density concrete. Barite may also find use as an aggregate material in concrete and in other applications as more knowledge of its characteristics is determined by research efforts.

Increased interest in barite and barium compounds in special applications, such as barium titanate in electrical systems, and barium silicide in gray iron production, may lead to larger markets.

Continued improvement in technical processes is anticipated. A commercial process has been developed for the successful separation of a barite-fluospar ore, providing a marketable grade of both mineral commodities. Such advances lead to increased reserves and utilization of previously undeveloped deposits.

Exploration for new deposits, development of new uses, and research directed toward increasing efficiencies in all steps of barite operations will continue.

PROBLEMS

The outstanding problem of the barite industry is its overwhelming dependence on a single market, the long-term stability of that market being somewhat speculative. Lack of comprehensive research on properties and prospective uses of barite and its derivatives is a retarding factor in developing new markets.

A major long-range problem of the domestic barite industry is that of maintaining a satisfactory reserve position, partly because reserves in residual deposits are difficult to measure. The need for additional barite deposits near major consuming areas is of particular concern, as is the reserve situation of barite suitable for use in chemical applications.

A continuing problem of domestic producers of both barite and barium chemicals is the need for increasing process efficiency to maintain their positions in the market. In some instances better beneficiation methods are needed to meet quality requirements.

To guide both industry and Government agencies in their activities concerning barite, more definitive commodity statistics are needed. The most serious deficiency is lack of statistical detail on end uses.

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BERYLLIUM

By Donald E. Eilertsen [1]

BERYLLIUM became commercially important in the United States in the late 1920's. Two U.S. companies are the world's largest consumers of beryl and producers of beryllium metal, alloys, and compounds; their combined sales in 1963 were almost $53 million. Three other companies have small beryllium operations. One of these firms produces small quantities of beryllium mineral flotation concentrate and beryllium compounds, another firm produces electrorefined beryllium from scrap, and the third firm imports and fabricates beryllium from France.

Beryllium has long been famous for its ability to harden copper with steellike strength; beryllium-copper alloys have many industrial applications.

In recent years the Government has become interested in the outstanding nuclear and physical properties of beryllium metal, and it has been subjected to comprehensive research and development. Many new uses for beryllium metal in nuclear energy, high-speed flight, missiles, and space exploration are developing from this research.

Hand-sorted imported beryl from pegmatites is practically the exclusive commercial source of beryllium; the resource of cobbable beryl in the United States is small and not much is known about the foreign resources. One of the pressing problems of the beryllium industry is uncertain resources for the increasing demands.

BACKGROUND

Beryllium, discovered in 1797, was first produced in 1828, simultaneously in France and Germany. The element was first called earth-of-beryl; later, it was called glucinium because of the sweet taste of some of its compounds, and finally the name beryllium was adopted.

The hardening effect of beryllium on copper was discovered in 1926, and its industrial use for this purpose began soon after. Beryllium also was found to have a high melting point and to be exceptionally strong and stiff, despite being nearly as light as magnesium. Another exceptional property, high penetrability by thermal neutrons, led to use in X-ray tube windows.

After World War II the unusual properties of beryllium led to intensive efforts to expand the supply of beryllium minerals and to develop processes to extract, refine, and utilize beryllium for highly specialized structural applications and other purposes. Partly successful, these research efforts are continuing, and seem likely to create a growing use for the metal and its compounds.

[1] Commodity specialist.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Practically no hand-sorted beryl is produced in the United States at present; all beryl for consumption is imported.

Only two companies in the United States process beryl into beryllium metal prdoucts: The Beryllium Corp., Reading and Hazleton, Pa., and the Brush Beryllium Co., Elmore, Ohio.

The Beryllium Corp.'s net sales in 1963 totaled $28.2 million. The firm produces beryllium metal, beryllium-copper, beryllium-nickel, beryllium-aluminum, beryllium-iron, and various beryllium compounds at Reading, Pa., and Beryllium metal at Hazleton, Pa. This company also has rolling, foundry, and fabricating facilities.

The Brush Beryllium Co.'s sales and service in 1963 totaled $24.3 million. This firm produces beryllium metal, beryllium-copper, beryl-

lium-nickel, beryllium-aluminum, and various beryllium compounds; it also has rolling, foundry, and fabricating facilities.

Three other consumers of beryl are Beryl Ores Co., Arvada, Colo., which produces specialized materials for the ceramic industry; Lapp Insulator Co., LeRoy, N.Y., which uses ground beryl in making high-voltage electrical porcelain; and Champion Spark Plug Co., Ceramic Div., Detroit, Mich., which uses beryl as a minor constituent in special ceramic compositions for spark plugs.

In recent years, Mineral Concentrates and Chemical Co., Inc., has produced small quantities of beryl-bertrandite-euclase flotation concentrate at its Tarryall flotation plant near Lake George, Colo.; the company has utilized some of this material to produce small quantities of various beryllium compounds at Loveland, Colo.

Beryllium Metals & Chemicals Corp. (a subsidiary of Lithium Corporation of America), Bessemer City, N.C., produces electrorefined beryllium from scrap beryllium.

Geneal Astrometals Corp. (mostly owned by The Anaconda Company), Yonkers, N.Y., fabricates beryllium imported from France.

Companies in the United Kingdom, Japan, and France process beryl to beryllium metal, alloys, and compounds.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Beryllium, the seventh lightest metal, has great stiffness, exceeding other metals including steels; desirable thermal properties, especially for heat-sink applications; a very high strength-weight ratio; and attractive nuclear properties. Some of its properties are atomic number, 4; atomic weight, 9.01; density, 1.84 grams per cubic centimeter; modulus of elasticity, 44 x 10^6 pounds per square inch; melting point, 1,285° C; specific heat, 0.4 calorie per gram per ° C; coefficient of thermal expansion, 11.54 x 10^{-6} centimeter per centimeter per ° C; thermal conductivity, 0.38 calorie per square centimeter per second; electrical conductivity, 40–45 percent of International Annealed Copper Standard; and reflectivity, 55 percent of white light. Beryllium is brittle. Some nuclear properties of beryllium are atoms per cubic centimeter, 1.24 x 10^{23}; neutron scattering cross section, 6.9 barns per atom; and neutron absorption cross section, 0.009 barn per atom.

Beryl ($3BeO \cdot Al_2O_3 \cdot 6SiO_2$) when pure contains about 14 percent beyllium oxide (beryllia or BeO) or about 5 percent beryllium metal (Be). Commercial beryl is hand-sorted or cobbed crystals and lumps of beryl usually containing about 11 percent BeO, or 4 percent Be.

Beryl is bought on a basis of short ton units of contained BeO, a unit being 1 percent of a short ton, or 20 pounds. The price per ton of beryl is determined by the number of short ton units of contained BeO in a ton of beryl, multiplied by the corresponding unit value for concentrate of that particular BeO content. The price may be computed quickly by multiplying the percentage of BeO by its corresponding unit value; for example, the price per ton of beryl having 11 percent BeO and a value of $25 per short ton unit of BeO would be $275.

Beryllium-copper master alloy contains 4 percent beryllium, the remainder being copper. This alloy is remelted with additional copper to obtain beryllium-copper alloys of lower beryllium content.

Toxicity (*2, 4*)[2]

Some forms of beryllium are known to be toxic, but many years of research are needed to learn about beryllium-associated diseases. No ill effects have developed in mining, storing, and transporting beryl, but precautions should be taken in handling some beryllium minerals, especially certain forms of bertrandite which are soluble in dilute acid and possibly sufficiently soluble in body fluids to cause dermatitis.

No one is known to have been poisoned from ingestion of beryllium compounds, or to have contracted dermatitis or pneumonitis from handling or mechanically working low-beryllium alloys such as beryllium-copper alloys. Dermatitis may occur from coming in contact with soluble beryllium compounds, and acute pneumonitis may develop from inhaling mists, dusts, or fumes from these compounds and from melting the metal and its alloys; the ill effects sometimes develop slowly over many years.

Modern control practices have practically eliminated new cases of beryllium disease. Much has been done by the beryllium industry to prevent the disease. Working places are kept clean, workers are required to wash their hands frequently, clothing is laundered regularly, dusts, fumes, and mists are caught at the source and deposited in dust collectors, and numerous other precautions including medical programs have been adopted to make working conditions safe.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

TECHNOLOGY

Mineralogy and Geology

The earth's crust is estimated to contain 6 parts per million (ppm) of beryllium, compared with 0.1 ppm of silver and 16 ppm of lead. Beryllium occurs as an essential constituent in approximately 40 minerals, and as an occasional constitutent in 50 other minerals (*6, 8*). Beryl, bertrandite, phenacite, barylite, and chrysoberyl are some of the most commonly known beryllium minerals, but beryl is practically the sole commercial source of beryllium.

The world's principal commercial sources of beryl are heterogeneous granite pegmatites, where the mineral occurs in enriched zones, filled fractures, and replacement bodies. Homogeneous pegmatites have yielded little beryl. The principal beryl deposits are found in zones that usually contain only a few thousand tons of pegmatite rock; however, some deposits contain a million tons or more of rock. Certain zones in some pegmatites contain more beryl than others. Sometimes beryl is found in shoots that are parts of zones. When beryl occurs in zoned pegmatites the largest crystals usually are near the core and the fine grained crystals near the outer zone.

Promising quantities of beryllium have also been found in various nonpegmatite deposits. At Spor Mountain, Utah, bertrandite occurs erratically in altered tuff associated with fluorite, montmorillonite, opal, and chalcedony. Similar deposits have been found in the Honeycomb Hills, Utah. In White Pine County, Nev., phenacite and bertrandite occur with scheelite, fluorite, pyrite, and other minerals in limestone. In Park County, Colo., beryl and bertrandite occur with fluorite in mica-quartz greisen along the contact with granite. At Seal Lake, Labrador, Canada, barylite occurs in veinlets with quartz and albite. In northern Coahuila, Mexico, bertrandite was found in fluorite which contained other minerals such as quartz, kaolinite, and hematite.

Mining

Occasionally pegmatites are mined for beryl alone, but more often beryl is recovered as a coproduct or byproduct while recovering other minerals such as feldspare, mica, lithum minerals, columbite, tantalite, and cassiterite. Deposits often contain less than 100 tons of cobbed beryl; however, some deposits yield several thousand tons of beryl.

Some pegmatite deposits are mined on a small scale, usually by crude opencut methods. Mining is begun on an outcrop where the minerals of value can readily be seen, and cuts are made or pits are sunk by drilling and blasting the rock. Hand-drilling methods are sometimes used in out-of-way places, but usually air-driven drills are used. The blasted rock is hand-cobbed to recover valuable minerals including beryl, and the waste rock is discarded.

The cycle of drilling, blasting, cobbing for valuable minerals, and hauling waste to dumps is repeated until the operation cannot be worked economically. Sometimes the blasted rock is coarsely crushed and passed over belts so that valuable minerals can be sorted from it. The balance of the rock may be reduced further in size for concentrating the associated valuable minerals. Where conditions warrant, mechanized mining methods are used.

Milling

Beryl, feldspar, and some other pegmatite minerals have densities so nearly the same that it is difficult to separate beryl by mechanical methods. Flotation methods have produced beryl concentrates on a laboratory scale, but it has been difficult to produce material on a commercial scale to equal the quality, price, and ease of obtaining hand-sorted beryl. Consequently, all commercial beryl is hand-cobbed, and seldom are crystals and fragments recovered less than 1 inch in size. Probably not more than one-third of the beryl in the average commercial deposit is recovered by the crude hand methods now employed.

Recent discovery of important resources of bertrandite in clay formations in Utah aroused great interest, and studies on this material indicate that hydrometallurgical procedures may have to be employed to extract beryllium compounds directly from the ore, because beneficiation methods do not appear to work satisfactorily.

Preparation of Beryllium Oxide and Beryllium

Several methods for converting beryl to beryllium oxide have been developed. The Copaux-Kawecki fluoride process is used by The Beryllium Corp., and the Sawyer-Kjellgren sulfate process is used by The Brush Beryllium Co.

In the Copaux-Kawecki fluoride process beryl containing 10 to 12 percent BeO is crushed, ground in a wet ball mill to minus 200-mesh, and filtered. It is then mixed in batches with soda ash, sodium silicofluoride, and sodium ferric fluoride and made into briquets. The briquets are dried, sintered, cooled, crushed, and ground in a wet pebble mill to which hot water is added,

and the slurry is pumped to a tank for leaching. More water is added and the mixture is agitated, leached, and allowed to settle. The liquid, containing soluble sodium beryllium fluoride, is decanted to separate it from the solids, which contain aluminum and iron oxides and silica. Caustic soda is added to the heated solution to precipitate beryllium hydroxide, which is filtered and calcined to convert it into beryllia (*1*).

The Sawyer-Kjellgren process is based on the discovery that if melted beryl is quenched in cold water the resultant frit reacts with sulfuric acid. The beryl, containing 10 to 12 percent beryllia, is crushed, dried, and melted in an electric arc furnace. The melted beryl is poured into water to obtain frit, which is dry-ground in a ball mill to a fine powder. Batches of the powder are mixed with concentrated sulfuric acid, steamed, and agitated. Water and more steam are then added to the slurry. The liquid, containing soluble beryllium and aluminum sulfates, is filtered from the sediment and pumped to a tank where ammonium hydroxide is added. The filtrate from this operation is further treated with a chelating agent to prevent impurities from precipitating upon subsequent addition of caustic soda. Hydrolysis follows, and the precipitate, beryllium hydroxide, is filtered off. This precipitate is ignited in an electric furnace to form beryllium oxide (*4, 9*).

The beryllium products of either the Copaux-Kawecki or the Sawyer-Kjellgren process generally have to be purified to produce beryllium metal.

The oxide or hydroxide can be dissolved in ammonium bifluoride solution and heated to boiling, and calcium carbonate flour is added to precipitate aluminum (*9*). Lead dioxide is added to remove manganese and chromium, and the resultant slurry is filtered through pressure filters using stainless steel screens precoated with rayon fiber. Lead, nickel, and copper are next removed from the filtrate with ammonium polysulfide. After being filtered again, the solution is evaporated, and pure ammonium beryllium fluoride is recovered by crystallization. This fluoride is then thermally decomposed to beryllium fluoride, while the ammonium fluoride is volatilized.

Beryllium metal is produced by the reduction of beryllium fluoride with magnesium metal. This is usually done in batches in a high-frequency induction electric furnace provided with a graphite crucible (*3–4, 9*). An excess of beryllium fluoride must be used to keep the highly exothermic reaction under close control. When reduction of the batch has been completed, the temperature is raised to about 1,300° C to melt the beryllium and allow it to coagulate into a pool at the surface of the slag. After cooling, the solid beryllium is separated from the slag, and the slag is leached to recover its beryllium content. The metal is remelted in a vacuum, which volatilizes slag occlusions and small amounts of impurities such as magnesium.

Preparation of Beryllium-Copper Master Alloy

To prepare beryllium-copper master alloy, weighed quantities of beryllium oxide, carbon powder, and copper are mixed in batches and melted in an electric arc furnace (*1*). The product is impure beryllium copper. Additional refining or other treatment removes the carbon and gases absorbed during reduction. The final product contains about 4 percent beryllium and is called beryllium-copper master alloy.

USES

One of the earliest uses for beryllium was as windows in X-ray tubes. Interest for beryllium grew rapidly with the coming of nuclear energy and the advent of high-speed aircraft, missiles, and space exploration. Beryllium's unique nuclear properties quickly attracted interest for testing and using the metal in nuclear reactors as moderator and reflector material, as neutron source material, and possibly as a canning material for fuel elements. Quantities of beryllium used in individual reactors range from a few pounds in Systems for Nuclear Auxiliary Power devices to 3,500 pounds in the Advanced Test Reactor; some reactors do not contain beryllium. Beryllium's unusual physical properties, especially high stiffness, high heat capacity, and low density, aroused substantial interest among scientists in 1957, and shortly thereafter extensive research and development began. Much of this work is still in progress.

Numerous uses for beryllium are gradually emerging from these intense studies. The metal is used in gyroscopes, accelerometers, parts of inertial guidance systems for high-speed flight and marine navigation, airplane brakes, heat shields such as those used in the *Freedom 7* and *Friendship 7* space capsules which orbited the earth, and shingles such as those used on the outside of the *Aurora 7* space capsule. Other applications for beryllium include a gold-plated beryllium antenna on *Telstar I*, intricate plates for Gemini (two-man) space capsules, large extruded tubing for the Project Saturn rocket program, and spacers, penetration aids, and various other sections in missiles. Recently reported uses include rotor blades and various other parts for gas turbine engines, solar cell mounting boards for satellites, and mirrors and

other optical parts. The winning car in the Indianapolis 500-mile race on Memorial Day 1964 had beryllium brakes. The list of uses for beryllium metal is growing; many important uses for beryllium are still on drawing boards or in the development stage. Among these is the use of beryllium for propulsion.

The industry was founded on the ability of beryllium to harden and strengthen some soft and ductile metals and alloys, and a major use for beryllium has been in this field. Most notable are the beryllium-copper alloys. These have many special qualities including high strength; excellent castability, formability, and machinability; high electrical and thermal conductivity; high resistance to corrosion and fatigue; stability under load; low creep-tendency; and antisparking and nonmagnetic qualities. Copper containing approximately 1.9 percent beryllium offers maximum strength and hardness; 0.4 percent beryllium, high conductivity; and 1.2 percent beryllium, midway properties. Some of these alloys contain small amounts of a third element such as nickel or cobalt. Beryllium-copper is available in wrought, cast, or forged form.

Beryllium-copper has a long list of uses; they include springs, bellows, diaphragms, electrical contacts, aircraft engine parts, plastic molds, marine propellers, gears, bearings and bearing retainer rings, shims, precision castings, and rollers. Beryllium-copper is also finding numerous applications in miniature electrical and electronic components.

Some new uses for the alloy include housings to protect undersea telephone systems, automobile starter springs, bucket wheels used in instruments to measure the velocity of water, and antennas for space vehicles and satellites. Space capsule *Sigma 7* contained an antenna consisting of tightly wound beryllium-copper ribbon that ejected to form a tubing 16 feet long. The *Lofti* and *Traac* satellites have this type of antenna. Other antennas were designed to eject as much as 1,000 feet of 0.5-inch-diameter tube from the ribbon.

Beryllium-nickel alloys are heat treatable and resemble stainless steels in many respects. Uses for beryllium-nickel alloys include surgical instruments, matrix for diamond drill bits, parts for fuel pumps and business machines, and dies for shaping aluminum channels, necks of bottles, stainless steel dinnerware, and plastics.

Beryllium also is used as an alloying constituent to improve the processing and properties of light metals. New beryllium-aluminum alloys containing mostly beryllium are available and are attracting attention.

Beryllium oxide has applications in nuclear reactors and in a wide variety of commercial applications, particularly ceramic parts for the electronic industry.

Besides being the commercial source of beryllium, beryl has ceramic applications in high-voltage electrical porcelains, suspension insulators, and spark plugs.

ALTERNATE MATERIALS

Uses for beryllium metal are gradually developing and it is quite likely that where beryllium has replaced other metals those metals can to a certain extent again be used in place of beryllium. Although beryllium has the lowest termal-neutron cross section of all the metals, magnesium, zirconium, aluminum, and stainless steel are alternate materials in the nuclear-energy field and each has superior qualities for certain applications.

An alloy containing 20 percent manganese, 20 percent nickel, and 60 percent copper is reportedly a good substitute for beryllium-copper in springs, diaphragms, and spark-resistant and antimagnetic tools, but not in applications where electrical conductivity is important.

Phosphor bronze can be used in place of beryllium-copper, particularly in manufacturing springs and diaphragms, but it is only about half as strong and half as conductive of electricity as 2 percent beryllium-copper. Aluminum bronze was used before the development of beryllium-copper alloys in making nonsparking tools, especially those which did not require cutting edges.

Aluminum bronze containing nickel can be hardened by heat treatment and is a fair substitute for beryllium-copper in cutting tools. Stainless steels and special alloy steels could be used in a few instances as substitutes, but none of these performs in all respects as well as beryllium-copper.

RESERVES

The beryllium reserves in the United States have been studied by the industry and Government for potential beryllium for many years, particularly since 1958. Although beryl reserves in pegmatites in the United States are fairly well known, there are few data on world reserves. The beryllium reserves of nonpegmatites are known for a few deposits; world deposits have received scant attention.

The U.S. reserves of beryl in pegmatites vary greatly with the grade and size of deposits (*5*). For example, one estimate shows a reserve of 8,800 tons of beryl (440 tons of beryllium) in deposits containing at least 1 percent beryl and at least 100 tons of beryl. Approximately 75 percent of this beryl is in New England and

South Dakota. Another estimate shows a reserve of 216,000 tons of beryl (10,800 tons of beryllium) in deposits containing 0.2 to 1 percent beryl and at least 100 tons of beryl. More than 90 percent of this beryl is in the tin-spodumene belt of pegmatites, 25 miles in length and up to 2 miles in width, extending through Kings Mountain, N.C. The pegmatites in this belt were reported to contain 823,000 tons of beryl (41,000 tons of beryllium) to a depth of 300 feet, the pegmatite containing about 8 pounds of disseminated beryl per ton of rock.

The world reserve of beryl in pegmatites is not known. An inquiry made in 1959 by the U.S. Government indicated that most countries that supply the United States with hand-sorted beryl could produce more beryl if needed and substantially more beryl if prices were higher. In many instances the investigation revealed that resources of hand-cobbed beryl were being depleted rapidly. Very few firm data on beryl reserves were obtained because the occurrence of this mineral is unpredictable.

In recent years interest has focused on nonpegmatitic sources of beryllium. Promising deposits of beryllium have been found in several localities, and those in the Spor Mountain area in Utah and the Mount Wheeler area in Nevada have aroused appreciable interest. Various firms are studying the feasibility of recovering commercial beryllium, particularly from the Spor Mountain deposits. Tentative estimates by the Geological Survey, U.S. Department of the Interior, indicate that tuff in the Spor Mountain area and quartz monzonite in the Gold Hill area in Utah exceed 15 million tons of ore containing 0.5 percent BeO (27,000 tons of beryllium). The Mount Wheeler area in Nevada was tentatively reported to contain 500,000 tons of bertrandite and phenacite ore containing 0.5 percent BeO (900 tons of beryllium). (7)

Other beryllium deposits that have attracted widespread attention are those in the Lake George district, at the western edge of the Pikes Peak granite batholith in Park County, Colo.

Elsewhere in the world, new nonpegmatitic beryllium deposits in Labrador and Mexico have attracted unusual attention. Deposits in the Seal Lake area of Labrador (about 100 miles northwest of Goose Bay) were tentatively reported to have 3 million tons of barylite ore containing 0.5 percent BeO (5,400 tons of beryllium). Deposits in the Aquachile area of Mexico (80 miles southwest of Marathon, Tex.) reportedly contain substantial bertrandite ore.

SOURCES OF STATISTICAL INFORMATION

Data on the domestic production and consumption of beryl and the production of beryllium metal alloys and compounds are collected by the Bureau of Mines through industry canvasses. Statistical data on imports and exports of beryl and beryllium products are obtained from the Bureau of the Census, U.S. Department of Commerce. Data on world production of beryl are compiled by the Bureau of Mines from information supplied by Foreign Service dispatches, from official publications of the mining departments of the respective countries, and from other sources. Enough statistical information is available at present on beryl, beryllium metal, alloys, and compounds for the present needs of the Government, industry, and the public.

PRODUCTION, CONSUMPTION, AND TRADE

Domestic production of hand-sorted beryl has always been small in the United States. Prior to 1953 the 15-year annual average was 255 tons, but during the following 10 years (1953–62) the annual average rose to 446 tons, mostly because the Government paid incentive and premium prices for domestic beryl during this period. Approximately 200 operations produced beryl in 1957. In 1963, after the Government stopped paying premium prices, only 1 ton of beryl was produced.

A total of 4,456 tons of domestic beryl was produced during 1953–62, and 3,276 tons of this was sold to the Government for incentive prices. The 14 States producing beryl during this period, in descending magnitude, were South Dakota, Colorado, New Mexico, Maine, New Hampshire, Connecticut, Georgia, Arizona, Wyoming, North Carolina, Maryland, New York, Idaho, and Virginia.

In addition to hand-cobbed beryl some select low-grade ore, mostly beryl-bertrandite-euclase, was produced in Colorado; the outputs were 42 tons in 1958, 97 tons averaging 4.44 percent BeO in 1959, 265 tons averaging 5 percent BeO in 1960, 805 tons averaging 3.37 percent BeO in 1961, 760 tons averaging 3.05 percent BeO in 1962, and 750 tons averaging 3 percent BeO in 1963.

During 1959–63, 22 countries produced beryl; the annual output ranged between 6,650 and 12,000. The eight largest producers were Brazil,

Argentina, Mozambique, the U.S.S.R., Uganda, the Malagasy Republic, Southern Rhodesia, and India.

Production data on outputs of beryllium metal, alloys, and compounds are company confidential.

Beryl consumptions in the United States during 1959–63 were 8,173 tons in 1959, 9,692 tons in 1960, 9,392 tons in 1961, 7,758 tons in 1962, and 7,934 tons in 1963. Almost all of this beryl was utilized to produce beryllium metal, alloys and compounds.

Beryllium ore and concentrate are imported duty free. Unwrought beryllium is dutiable at 17 percent ad valorem; beryllium-copper master alloy, 1.275 cents per pound plus 20 percent ad valorem; and beryllium oxide and carbonate, 10 percent ad valorem.

Import and export data on beryllium for 1959–63 are shown in table 1.

TABLE 1.—*Beryllium imports and exports*

Year	Imports [1]		Exports [2]			
	Beryl (short tons)	BeO or $BeCO_3$ (pounds)	Beryl (short tons)	Beryllium and beryllium alloy (except beryllium-copper) metal powders (pounds)	Beryllium metal and alloys (except beryllium-copper) in crude form and scrap (pounds)	Beryllium and beryllium alloys in semi-fabricated forms, n.e.c. (pounds)
1959	8,038	906	----------	5,519	153,428	5,313
1960	8,943	2,603	7	9,166	102,264	6,062
1961	8,516	3,281	----------	1,815	120,830	692
1962	8,552	19	----------	1,260	60,468	1,217
1963	6,243	200	1	6,015	93,034	774

[1] Data on unwrought and wrought beryllium imports were not available prior to September 1963.
[2] Separate data on beryllium-copper alloy exports were not available.

Starting in September 1963, additional data on beryllium imports became available. These additional imports for September–December 1963 were 2,110 pounds of other beryllium compounds, 31,888 pounds of unwrought, waste, and scrap beryllium, and 13 pounds of wrought beryllium.

STRATEGIC CONSIDERATIONS

The beryllium industry depends wholly on imported beryl for its commercial source of beryllium.

Beryl and beryllium-copper master alloy are stockpiled under the Strategic and Critical Materials Stockpiling Act of 1946 (Public Law 520, 79th Congress). Both the basic and the maximum objectives of this program have been achieved.

Government inventories of beryl, beryllium, and beryllium-copper master alloy on December 31, 1964 are shown as follows:

Material	Strategic stockpile, stocks	Defense Production Act, stocks	Commodity Credit Corporation, stocks	Supplemental stockpile, stocks	Total stocks
Stockpile-grade beryl, tons	23,230	2,086	[1] 6,183	18,212	[1] 49,711
Nonstockpile-grade beryl, tons	----------	456	----------	----------	456
Upgraded materials from some of the above stockpile-grade beryl:					
Beryllium-copper master alloy, tons	1,075	----------	6,312		7,387
Beryllium metal, tons	----------	----------	153		153

[1] Includes 6,000 tons of beryl on order.

GOVERNMENT PROGRAMS

The Office of Minerals Exploration, U.S. Department of the Interior, offers financial assistance up to 50 percent of approved costs to explore for all types of beryllium ore.

Under the Agricultural Trade Development and Assistance Act of 1954 (Public Law 480, 83d Cong.) The Commodity Credit Corporation, U.S. Department of Agriculture, occasionally barters surplus agricultural commodities with certain countries for strategic materials including beryl, beryllium, and beryllium-copper for the supplemental stockpile.

PRICES

Prices for domestic and imported cobbed beryl are on a buyer and seller basis. The average price of imported beryl containing approxi-

mately 11 percent BeO at ports of exportation for 1964 was $253 per short ton, or about $23 per short ton unit of BeO.

In December 1964 American Metal Market quoted the price of beryllium metal, 97 percent pure, beads, f.o.b. Reading, Pa., and Cleveland, Ohio, at $62 per pound in 1,000- to 2,000-pound quantities. A blend of beryllium powder, 200-grade, was quoted at $54 per pound in quantities of 20,000 pounds. Vacuum-cast beryllium ingot was quoted at $67 to $71 per pound. Beryllium-copper master alloy was quoted f.o.b. Reading, Pa., Detroit, Mich., and Elmore, Ohio, at $43 per pound of contained beryllium with copper paid for at the market price on date of shipment. Beryllium-copper strip, rod, bar, and wire were quoted at $2.04 per pound. Beryllium-aluminum was quoted at $65 per pound of contained beryllium with aluminum paid for at the market price. Beryllium-magnesium-aluminum was quoted at $60 per pound of contained beryllium with magnesium and aluminum paid for at the market price.

The Brush Beryllium Co. quoted the prices of UOX and GC–R beryllium oxide powders, minus 20-mesh and dry screened, at $12 to $15 per pound, depending on the quantity.

TAXES

Depletion allowance is 23 percent for domestic producers of beryl and 15 percent for U.S. producers in foreign countries.

RESEARCH

Beryllium metal has been undergoing thorough research in recent years. Industry and the Government, especially the Atomic Energy Commission, Armed Forces, and U.S. Department of the Interior, have kept beryllium high on the list of materials for intensive study, the subjects of which range from resources through extraction, purification, fabrication, properties, and development of uses. Much of the research has been completed, but much remains to be done. Bureau of Mines work on beryllium has included a nationwide study of the beryllium potential in domestic mineral resources and research on the development of mineral beneficiation methods and on methods to extract, purify, and fabricate beryllium, the resource studies being almost completed. Numerous Reports of Investigations have been published.

OUTLOOK

Extensive research and development have been underway on beryllium since 1958 and will strongly influence the use pattern and growth rate of the beryllium industry. Commercial use of beryllium and its alloys will expand moderately, but the major short-term growth of beryllium metal will be in defense, atomic energy, and space exploration applications.

The hand-sorted beryl supply may be inadequate to satisfy long-term and greater demand for beryllium alloys, compounds, and metal. In the near future beryllium will probably be extracted directly from bertrandite ore or from mill concentrate of beryl, phenacite, bertrandite, or other beryllium minerals in sufficient quantity to supplement imported hand-sorted beryl.

Attention will be directed increasingly to the world's potential resources of beryllium in low-grade deposits, and the expectation is that deposits will be found and developed in the United States that will be able to fulfill domestic needs in an emergency. It is not clear whether U.S. deposits now known will be commercially competitive with foreign beryl mines, because there is too little knowledge of the extent and grade of resources in other countries.

International competition for beryllium markets may become more noticeable when demands for beryllium products increase.

PROBLEMS

A main problem of the industry is to determine how best to gain advantage of newly discovered qualities of beryllium in finished products. Much more diversified use of beryllium is needed to fully determine uniformity of mill products and advantages for using the metal. Currently produced beryllium is brittle and reported to be ready for prototype structural elements but not for large-scale use in major aircraft components.

In seeking to develop additional beryllium supplies, it should be recognized that longtime adequacy of supply from hand-cobbed beryl derived from pegmatite deposits has dulled commercial interest in other, less easily recognizable sources. Until recently, knowledge of beryllium occurrences has not been sought intensively. Comprehensive detailed knowledge of the nature of beryllium concentrations in the earth's crust is needed. Vigorous and rapid

pursuit of this problem is warranted, since all discoveries are potential commercial competitors, and new information may profoundly influence decisions based on prior knowledge. As facts are found, intensive exploratory efforts may be assigned to the most promising discoveries.

The attractive combination of properties that beryllium apparently offers as a structural material has tended recently to detract attention from possible uses of the element in compounds and alloys. For example, beryllium oxide is of special interest both as a source of the metal and because of its refractory and nuclear properties. Great demands for beryllium products would intensify the resource and mining problems and would compel turning to poorer deposits for supply, thus increasing the difficulties of the extractive metallurgists.

Dusts and fumes from beryllium and numerous beryllium compounds are toxic to humans, and great caution must be exercised when one is exposed to these substances.

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BISMUTH

By Donald E. Moulds[1]

BISMUTH, known initially for its medicinal properties, today is noted chiefly for its metallurgical ability to impart desirable qualities of fusibility, castability, and machinability to a wide variety of industrial alloys.

The metal is obtained as a byproduct in processing ores of other metals containing minor quantities of bismuth. Byproduct sources have provided an increasing supply in recent years to meet the world requirement of over 6 million pounds annually. Peru, Mexico, Bolivia, Canada, and the Republic of Korea are the major suppliers of bismuth in ores, and concentrates. Several other countries, such as Japan and the United States, are large producers of refined metal from imported raw materials.

The United States is the largest consumer of bismuth and is dependent on foreign sources for some 90 percent of its requirements, either in the form of imported base metal ore and bullion or in the form of refined metal and alloys. Peru, Mexico, and Canada are the chief suppliers to the United States. Three lead refineries currently produce all of the domestically refined bismuth.

The degree of dependence on foreign sources of supply and the many essential industrial and medicinal uses classify bismuth as a strategic and critical material. Inadequate data on domestic production and bismuth content of domestic ores hamper determination of domestic bismuth potential.

The outlook for bismuth is one of continued growth in consumption, especially in the field of industrial alloys and chemicals, in step with rising national industrial activity. Development of new applications is expected, but these are not anticipated to require large quantities of bismuth.

BACKGROUND

The association of bismuth with ores of other metals and its affinity for these metals in medieval metallurgical processes caused the white substance found with lead and tin in smelting to be referred to by early writers as imperfect tin, as female antimony, or as an imperfect form of lead.

Undoubtedly bismuth-lead and bismuth-tin alloys formed in conjunction with lead and tin metal were recognized and used prior to the Middle Ages. In the 15th century Basil Valentine referred to the substance as "wismuth," and at the end of the 16th century Georgus Agricola, the early mineralogist, latinized the German name to "bisemutum." About 1597, the efficacy of bismuth nitrate in treatment of intestinal disorders was discovered by Andreas Libavius. It was not, however, until the 18th century that J. H. Pott, C. J. Geoffrey, and T. Bergman produced the pure metal, demonstrating it to be a distinct element similar in many respects to lead (*3*).[2]

Bismuth initially was produced by smelting bismuth-rich ores with suitable fluxes to produce a crude metallic bismuth. The association of bismuth with base metal ores and the fact that it accompanies lead through the smelting and refining operation has permitted extraction to be concentrated at lead refineries. Beginning in 1833 with the Pattison process for debismuthizing lead bullion (*6*), continued development and improvement of metallurgical processes for extraction and purification of bismuth have resulted in a commercially available bismuth metal of 99.995-percent purity.

Bismuth as a compound was noted initially for its soothing effect on human digestive disorders and its healing effect on wounds and sores. This property of bismuth was exploited in many medicinal and cosmetic preparations, which up to 1930 used some 90 percent of the bismuth consumed. The development of low-melting alloys has resulted in a wide variety of industrial applications of bismuth alloys and chemical compounds. While advances in medical technology have made many medical uses of bismuth obsolete, the industrial and chemical developments have resulted in a continuing growth in consumption.

[1] Commodity specialist.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

World production of bismuth is about 6.5 million pounds annually. As output is derived as a byproduct of processing ores of other metals, the bismuth-producing industry is distributed among all of the countries having metal-refining facilities. The major producing countries are Bolivia, Canada, Japan, Mexico, Peru, the Republic of Korea, and the United States. Approximately three-fourths of the world supply is contributed by these countries; Peru is the largest supplier with some 20 percent of free world output. United States production of refined bismuth is confined to three companies operating bismuth refineries in conjunction with lead refining plants; American Smelting and Refining Company, Omaha, Nebr., United States Smelting Lead Refinery, Inc., East Chicago, Ind., and United Refining & Smelting Co., Chicago, Ill.

Bismuth is consumed in the manufacture of products in all of the industrial nations. While consumption statistics are not available on a comparative basis, the United States is the leading consumer with requirements approximately one-third of world production. Other large consuming countries are those of Western Europe, Japan, and the U.S.S.R. The industry can be roughly divided into companies manufacturing chemical compounds and companies manufacturing alloys. Bismuth is consumed in 23 States with New York by far the largest consuming area. Some 60 companies predominantly in the eastern and Mississippi Valley industrial areas account for over 80 percent of the annual consumption.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Bismuth is a soft, heavy, coarsely crystalline metal having a tinny or silvery-white color tinged with red. Its atomic number is 83 and its atomic weight is 209. The specific gravity is 9.80 at 20° C. but is 10.067 in the molten state. Pure bismuth boils at 1477° C. but its melting point is low (271° C.), and it forms alloys with lead, tin, antimony, cadmium, and indium which melt at temperatures as low as 47° C. The thermal conductivity of solid bismuth is less than that of any other metal except mercury. Similarly, it is a poor conductor of electricity and is the most diamagnetic metal known. Its absorption cross section for thermal neutrons is the lowest of all metallic elements except beryllium (*3*).

The term "bismuth" commonly refers to refined metal; although there are no standard specifications, cast bismuth often assays 99.999 percent pure. The pharmaceutical trade employing bismuth for medical purposes demands a minimum purity of 99.99 percent and absolute freedom from arsenic. The following is a typical chemical analysis of commercially available bismuth:

	Percent
Bismuth	99.995
Lead	.0001
Copper	.0002
Silver	.0001
Iron	.0001

National Stockpile Specification P–7, which covers metallic bismuth suitable for production of bismuth-bearing alloys and bismuth salts, requires that all material shall have a minimum bismuth content of 99.99 percent.

TECHNOLOGY

Geology

It is estimated that the bismuth content of the earth's crust is 1 part in 10 million. Compared with aluminum, bismuth is indeed a rare metal. The composition ratio is about 2.5 pounds of bismuth to 1 million pounds of aluminum. Despite the quantitative scarcity, the frequency of occurrence of bismuth is remarkably high. The bismuth minerals, bismite (Bi_2O_3) and bismuthinite (Bi_2S_3), are widely distributed in small quantities in ores throughout all the continents. Native bismuth is not an uncommon constituent of hydrothermal veins in some mining localities such as Cordoba Province, Spain.

Because of the uneconomic concentration of bismuth in nature, practically no deposits can be mined for the bismuth content alone. Most is produced as a byproduct from mining and processing ores of lead, copper, tungsten, gold, and other metals containing minor quantities of bismuth.

Metallurgy

Bismuth minerals occasionally occur in sufficient quantity so that upgrading by hand sorting or gravity and flotation methods results in a bismuth-rich concentrate. Bismuth occurring as a sulfide or carbonate can be recovered from these concentrates by direct smelting in a reverberatory furnace with suitable fluxes to produce a crude metallic bismuth, matte, and slag. The crude bismuth requires further refining, while the matte is resmelted. Bismuth occurring as an oxide or carbonate commonly is recovered by leaching the ore with hydrochloric acid in earthenware vats and precipitating bismuth oxychloride by diluting the pregnant solution with water. Repeated cycles of

dissolution, precipitation, and removal of copper with scrap iron yield a purified oxychloride which is melted with charcoal and lime to yield a crude metallic bismuth for further refining. This method is also commonly used for recovery of bismuth from roasted tin concentrate and other bismuth-bearing materials.

Ore-dressing procedures employed for concentration of lead and copper minerals prior to smelting also concentrate the associated bismuth minerals. In many respects, bismuth acts similarly to lead in the usual smelting operations employed in treating copper and lead ores and thus collects with the lead. In the copper smelter, the lead and bismuth are volatilized and accompany the dust and fume produced by the melting furnace and converter. Copper smelters that treat ores containing lead and bismuth are usually equipped with a baghouse or a Cottrell precipitator to collect the dusts and fume. These products are then sent to the lead-smelting plants for treatment. The bismuth in lead ores, concentrates, and flue dust and fume is collected in the lead bullion during lead-smelting operations. Bismuth is considered to be a detrimental impurity in refined lead and if present in excessive amounts must be removed before the lead can be used for many applications (*1*).

The two most important methods used to remove bismuth from lead bullion are the Betts process and the Betterton-Knoll process (*2*). In the Betts process, cast anodes of lead bullion are electrolyzed in a lead fluosilicate to yield a pure lead cathode and an anode residue containing bismuth. The residue is melted to produce a metal alloy and a slag. The alloy containing the various metals is selectively oxidized to remove arsenic, antimony, and lead while the bismuth remains in the slags. The bismuth-rich slag is fluxed and reduced with carbon to a copper matte and crude bismuth metal.

In the Betterton-Knoll process used for recovery of over 90 percent of U.S. production, the lead bullion is first softened and desilverized by the Parkes process (*5*) to remove a silver-zinc insoluble segregate. Magnesium and calcium are added to the melt, the mass is cooled to near the melting point of lead, and a high-melting calcium-magnesium-bismuth dross is removed. The dross is liquated to melt as much entrained lead as possible; the residue is melted in a reverberatory furnace, treated with chloride or molten chlorides to remove the calcium and magnesium, and cast as lead-bismuth bullion.

The bismuth bullion or crude bismuth is melted and the contained arsenic, tellurium, copper, silver, and gold are removed by addition of suitable fluxes and by temperature control. The final refining of the bismuth is accomplished by treatment with chloride to remove zinc and lead as a dross. The bismuth metal is covered with molten caustic soda and cast as refined bismuth. This method of refining results in a bismuth metal of a purity up to 99.999 percent.

USES

Approximately 60 percent of the bismuth consumed in the United States is used in the manufacture of alloys. The most useful of these are the so-called fusible alloys. Bismuth is the chief ingredient, varying in quantity from 40 to 99 percent. Fusible alloys are used in a number of safety devices such as plugs for compressed-gas cylinders, automatic sprinkler systems, fire-door releases, electrical fuses, and ammunition solders. Other uses of low-melting-point alloys are in dental work, tool-tempering baths, fabric-dyeing baths, and pattern-making and tool-anchoring devices.

Bismuth is used in increasing quantities to improve the machinability of aluminum alloys and malleable irons and steels. Addition of small quantities increases the cutting qualities of the alloy without great sacrifice of important properties such as strength, toughness, and corrosion resistance. Extended life of the cutting tools and decreased cutting time greatly lowers unit cost of machined pieces produced from the bismuth-doped alloys.

In addition to their low fusibility, bismuth alloys possess several other distinct and useful properties. Like water, bismuth expands on passage from the molten to the solid state. This characteristic is imparted to many of the metal's alloys. In the bismuth-lead-tin system, structural changes after solidification cause further volume growth. Proper blend of the constituents yields alloys in which expansion may offset thermal contraction, yielding a casting of the precise dimensions of the mold.

Precision duplication also is fostered by the low surface tension of bismuth-alloy melts. High fluidity permits complete filling of the mold, even in molds having complex reentries.

The other major use of bismuth is as an ingredient in the manufacture of a wide variety of medicinal and industrial compounds. Some important bismuth compounds are the trioxide, hydroxide, trichloride, subcarbonate, subchloride, subiodide, nitrate, citrate, subsalicylate subgallate, and sulfocarbonate. Various compounds, salts, and mixtures of these are used for indigestion remedies, antacids, burn and wound dressings, antisyphilitics, dusting power, and cosmetics.

Insoluble salts of bismuth are given to patients before X-ray examination of the digestive tract. Bismuth trichloride is claimed to render some waterproofing materials, such as tar, creosote, and nondrying oils, less flammable. Bismuth trioxide has been used to a limited extent in vitreous enamels, porcelain, and glass, chiefly as a flux to increase the fusibility of coloring oxides or compounds. In these uses it resembles lead oxides but has the advantage of being nonpoisonous.

Experimental work consumes a significant amount of bismuth in the continuing scientific search. New applications together with other undefined uses represent 1.5 percent of the total annual consumption.

BYPRODUCTS AND COPRODUCTS

All bismuth produced in the United States is a byproduct of mining, smelting, and refining of other metals and ores, predominantly lead and copper, containing relatively small quantities of bismuth. Metallurgical affinity of bismuth for lead and the economics of byproduct processing cause the source material to collect and be extracted at primary lead refineries.

ALTERNATE MATERIALS

Despite many possible substitutes, bismuth holds a relatively stable position in most of its areas of use. Pharmaceuticals are the most vulnerable. Kaolin performs functions similar to those of many bismuth preparations. Antibiotics have substituted for others. Special plastics, resins, and alloys of other metals may substitute for bismuth alloys that are valued for precision casting and low fusibility. However, under present technologic and economic conditions bismuth remains the favored commodity.

SECONDARY SOURCES AND RECOVERY

Although many of the fusible alloys are reused by the original purchaser, traffic in bismuth scrap is small. That which does enter commerce reenters fusible alloys, bypassing the metal production stage. Availability of scrap limits secondary bismuth output.

Spent industrial chemicals and overaged pharmaceuticals are treated to recover the metal content. Fusible alloys such as those used in bending airframes and in anchoring tools are remelted and used repeatedly. Although secondary processing is insignificant, there is a large demand for scrap.

RESERVES

Because ultimate recovery of bismuth generally is as a byproduct of lead smelting, estimation of the recoverable resource is a function of the relationship of bismuth production and smelter production of lead projected on the estimated lead resources. The world bismuth resource is thus inferred to be at least 112 million pounds of recoverable metal, of which the United States would contribute 10 million pounds.

The principal foreign sources in order of importance are the copper, lead, and silver deposits of Peru, the lead deposits of Mexico, the tin and tungsten deposits of Bolivia, the lead-zinc ores of western Canada, and the tungsten ores of the Republic of Korea. The principal domestic sources are the lead-silver ores of Utah and Colorado and the copper-lead-zinc ores of Montana, Utah, Nevada, Arizona, Idaho, and New Mexico. Some gold ores of Idaho, Montana, Nevada, Alaska, Colorado, and other States contain minor quantities of bismuth, but it is not ordinarily recovered.

SOURCES OF STATISTICAL INFORMATION

The Bureau of Mines collects and tabulates data on production, consumption, and stocks of refined bismuth on a quarterly schedule. The Bureau also collects data informally on imports of bismuth-containing intermediate smelter products that are used directly by the consuming industry or that serve as source material for domestically refined bismuth production. There are numerous foreign publications that give fragmental statistics on production and consumption. Information on imports of refined bismuth is obtained from the U.S. Department of Commerce, Bureau of the Census. Exports of bismuth metal and alloys are also reported by the Bureau of the Census, but data are in terms of gross weight rather than contained bismuth.

The statistical sources for bismuth metal are adequate for the purposes to which the data are applied. Data on imports of bismuth alloys and bismuth-lead bars are, however, inadequate to provide a comprehensive picture of the industry.

PRODUCTION, CONSUMPTION, AND TRADE

Domestic production of refined bismuth is derived from intermediate smelter products of high-bismuth content collected in smelting of domestic and foreign ores and recovered at lead refineries. Production is confined to three

companies: American Smelting and Refining Co., United States Smelting Lead Refinery, Inc., and United Refining & Smelting Co. Quantitive production data supplied to Government are company confidential and therefore not available for publication. World production of bismuth by countries is shown in table 1.

World consumption statistics are not available by countries but the rising demand reflected in statistics of the United States undoubtedly applies to other industrial countries of the world and approximate the expanding supply availability. The United States is by far the largest consumer and in 1963 required about one-third of the world production. Salient statistics of bismuth in the United States are presented in table 2 and uses of bismuth in the United States is shown in table 3.

TABLE 1.—*World production of bismuth, by countries* [1] [2]

[Pounds]

Country [1]	1954–58 (average)	1959	1960	1961	1962	1963
North America:						
Canada (metal) [3]	308,633	334,736	423,827	478,118	425,102	380,285
Mexico [3]	831,800	527,600	599,400	[4] 140,000	780,000	[5] 948,000
South America:						
Argentina (in ore)	[5] 28,200	[5] 40,000	[5] 14,900	[5] 8,600	7,100	[5] 7,100
Bolivia [6]	124,910	487,400	403,700	465,300	652,300	[5] 504,600
Peru [3]	743,510	737,617	908,438	1,031,795	1,084,227	1,243,000
Europe:						
France (in ore)	83,600	101,400	112,400	116,800	[5] 116,800	[5] 110,000
Spain (metal)	91,914	53,168	29,875	21,427	18,799	[5] 18,700
Sweden [5]	115,100	66,000	79,000	79,000	154,000	155,000
Yugoslavia (metal)	221,174	200,026	231,582	216,348	199,765	[5] 194,657
Asia:						
China (in ore)	[5] 313,000	(7)	(7)	(7)	(7)	(7)
Japan (metal)	146,280	223,187	261,089	422,326	572,841	[5] 660,000
Korea, Republic of (in ore)	275,100	227,000	317,000	333,000	353,000	[5] 350,000
Africa:						
Mozambique	3,254	22,900	30,000	38,800	13,900	13,900
South Africa, Republic of (in ore)	767	527	511	168	130	[5] 770
South-West Africa (in ore)	1,300	530	310	485	155	[5] 5,100
Uganda	4,380	19,140	3,640	1,430	110	[5] 110
Oceania: Australia (in ore)	2,600	925	265	900	97	----------
World total (estimate) [1] [2]	4,600,000	5,000,000	5,300,000	5,100,000	6,700,000	6,500,000

[1] U.S. figure withheld to avoid disclosing individual company confidential data; included in world total. Bismuth is believed to be produced in Brazil, East and West Germany, and U.S.S.R. Production figures are not available for these countries, but estimates are included in the world total.
[2] This table incorporates some revisions. Data do not add exactly to totals shown because of rounding where estimated figures are included in the detail.
[3] Bismuth content of refined metal and bullion plus recoverable content of concentrates exported.
[4] In addition, approximately 2,000,000 pounds of bismuth in impure bars are excluded from the world total to avoid duplication.
[5] Estimate.
[6] Content in ore and bullion exported, excluding that in tin concentrates.
[7] Data not available; estimate included in world total.

TABLE 2.—*Salient bismuth statistics*

[Pounds]

	1954–58 (average)	1959	1960	1961	1962	1963
United States:						
Consumption	1,471,600	1,598,000	1,527,300	1,478,400	1,909,500	2,175,000
Imports, general	728,639	457,163	1,167,019	798,518	816,190	1,123,466
Exports	220,665	179,744	156,636	167,166	118,056	32,293
Price: New York, ton lots	$2.25	$2.25	$2.25	$2.25	$2.25	$2.25
Stocks Dec. 31: Consumer and dealer	327,500	472,000	362,800	323,000	447,800	428,100
World: Production	4,600,000	5,000,000	5,300,000	5,100,000	6,700,000	6,500,000

TABLE 3.—*Bismuth metal consumed in the United States, by uses*

[Pounds]

Use	1962	1963	Use	1962	1963
Fusible alloys	[1] 795,588	763,862	Experimental uses	5,212	6,433
Other alloys	442,040	572,543	Other uses	21,559	23,817
Pharmaceuticals [2]	645,149	808,383	Total	1,909,548	2,175,038

[1] Includes 159,188 pounds of bismuth contained in bismuth-lead bullion used directly in the production of an end product in 1962 and 168,137 pounds in 1963.
[2] Includes industrial and laboratory chemicals.

Imports form a large segment of the United States bismuth supply. In 1959–63, yearly receipts of refined bismuth from foreign countries averaged 872,000 pounds and furnished over 50 percent of the total metal available for consumption. Peru supplied 63 percent, Mexico 20 percent, Canada 9 percent, and Yugoslavia 5 percent, the remaining 3 percent was shipped from many other countries in Europe and Asia.

Metal imports are augmented by substantial quantities of bismuth that enter the United States as minor constituents of base bullion, in ores other than bismuth, and as impure bismuth-lead bars. The economically recoverable bismuth content of the ores and bullion enters the market as domestically refined bismuth. Most of the bismuth-lead bars, however, are consumed directly in alloy fabrication. Statistics relating to this category of imported bismuth are not formally collected by the Government. In some years estimates have been about 0.5 million pounds.

The United States is not traditionally an exporter of bismuth, but in years of slack industrial demand the rather inflexible nature of domestic production makes overseas sales desirable. The European market customarily is willing to absorb U.S. surpluses. Because economic cycles in Europe are often out of phase with those in the United States, domestic bismuth users occasionally absorb European surpluses.

Tariff on refined bismuth metal is 1⅞ percent ad valorem, effective since October 7, 1951, pursuant to concessions under the General Agreements on Tariffs and Trade. Chemical compounds, mixtures, and salts of bismuth are dutiable at 28 percent ad valorem, a rate that has applied since August 31, 1963. Bismuth ores and concentrates are entered duty free. The bismuth content of intermediate smelter products, such as base bullion, is dutiable on base metal content. Industrial alloys are dutiable at 18 percent ad valorem.

STRATEGIC CONSIDERATIONS

The degree to which the United States depends on foreign supply and the importance of precision castings and low-melting point alloys qualify bismuth as a strategic material. The United States holds stocks of the metal in the national and supplementary stockpiles to meet presently anticipated emergency requirements.

Approximately half of the U.S. yearly requirements of refined bismuth is imported. In addition, it is estimated that half of the domestic output of refined bismuth is derived from source materials of foreign origin. A substantial quantity of the Nation's bismuth needs enters the country in forms that bypass the metal stage, entering directly into alloy fabrication. It is estimated that 90 percent of the U.S. annual bismuth requirements originate abroad.

GOVERNMENT PROGRAMS

Under various congressional authorizations in times of national need the Government has stockpiled bismuth, controlled prices, allocated supply, and explored for domestic ore deposits. Exploration assistance is presently available under the program of the Office of Minerals Exploration with Government participation limited to 50 percent of the approved cost.

Under authority of the Stock Pile Act of 1946 and supplemental legislation the Government maintains an inventory of refined bismuth sufficient to meet emergency military needs. On June 30, 1964, inventories of refined bismuth totaled 3,835,000 pounds, of which 1,306,000 was in the national (strategic) stockpile, 23,000 pounds in Defense Production Act stocks, and 2,506,000 pounds in the supplemental stockpile. The total in the stockpile represented 106 percent of the presently anticipated emergency requirements.

In accordance with the Agricultural Trade Development and Assistance Act, the Commodity Credit Corporation may barter domestic surplus farm products for foreign bismuth metal.

PRICES

At the beginning of 1939, the New York price for refined bismuth metal was $1 per pound. Late in 1939 the price advanced to $1.25 per pound, where it remained until July 19, 1946. From that date until September 4, 1950, the average price was $1.95 a pound. On September 5, 1950, the price advanced to $2.25 a pound, in ton lots, where it remained until July 10, 1964, when it rose to $2.35.

TAXES

Depletion allowance for domestic producers of bismuth is 23 percent, and for U.S. producers with production in foreign countries, 15 percent.

TRANSPORTATION

Transportation costs are not a significant factor in the nationwide use of bismuth metal or alloys. Bismuth is sold in 6-, 10-, 22-, and 25-pound bars, the wholesale lot being 2,000 pounds. Bismuth bars are packed in cartons or wooden boxes protected with steel strappings. Wedges often are placed between the bars to prevent damage or breakage.

RESEARCH

The fundamentals of bismuth have been extensively studied and experimental research has developed a wide variety of industrial applications. The requirements of nuclear and astronautic developments offer a real incentive for scientific research on the potentialities of bismuth.

Research conducted by producers is primarily concerned with development and expansion of industrial markets for bismuth. Many broad industrial applications are attributed to basic experimental work sponsored by producers to exploit the unique properties and performance of the metal.

Consumers' research is more specialized, being confined to experimentation and development of special-purpose applications. Recent research concerned with thermoelectric energy conversion, using bismuth in combination with other junction materials, and with use of liquid metal cathodes has been promising. Nuclear uses are being investigated both as coolants and as a thermal neutron absorbant.

The Bureau of Mines has recently conducted research and published data on high-temperature heat, energy, and entropies of bismuth metal and bismuth compounds (*4, 7*).

OUTLOOK

The unusual and versatile properties of bismuth will continue to attract a comparatively large industrial research effort with a real possibility that substantial contributions will be made toward developing industrially important new technologic devices, methods, and products. Prospective new uses in thermoelectric elements and in chemicals are of major interest.

While the phenomenal rate of gain in consumption registered in 1962–63 is not expected to continue, a long-term growth potential of 3 percent annually, along with expected industrial growth, will require an estimated 2.5 million pounds of new metal supply for the United States by 1970.

The byproduct relationship of bismuth to production of other metals, as well as the relatively small quantity of bismuth recovered in relation to the host metals, imposes limits to which output can be expanded to meet increased demand. The currently improved outlook for host metal production and the presently indicated world overproduction capability predicate, however, an adequate supply to meet demand at a relatively stable price.

The supply-demand base for bismuth, measured in millions of pounds, does not provide the supply capability to meet rapid rise in demand resulting from a radically new and sizable use. Displacement of present market outlets and attendant price rises would necessarily follow, alleviated only to a small extent by high-cost bismuth ore production.

PROBLEMS

The primary commodity problem associated with bismuth is the dependence on foreign sources for the bismuth required to meet current and future industrial requirements.

Since the present supply is closely linked to and limited by resources and production of lead and copper, bismuth supply varies according to the demand for those metals rather than according to the independent requirements of bismuth. The relatively limited and inflexible supply thus restricts consideration of the useful and distinctive properties of bismuth for applications requiring substantial quantities.

Supply is vulnerable, especially in the strategic and mobilization areas, because of the lack of domestic bismuth deposits and base metal ores of high bismuth content, dependence of domestic refinery production on the bismuth content of imported base-metal ores and intermediate smelter products, and concentration of refinery capacity.

Inadequate information relative to several facets of the bismuth industry has impeded understanding of the supply-demand situation. The lack of information on the various components of domestic bismuth refinery production limits understanding of domestic supply potential. Basic knowledge of domestic source materials and contributing domestic mine sources is essential toward development of a program to improve the domestic resource base.

Although bismuth has been favored with substantial scientific attention and research development, problems exist in the application of bismuth in the nuclear and thermoelectric fields.

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BITUMINOUS COAL

By Staff, Division of Bituminous Coal

In establishing high standards of living and assuring continuity of industrial progress, energy has played a leading role. Of all the fossil-fuel sources of energy, coal is the most abundant.

Over millions of years, decaying plant material in swampy areas was transformed into various ranks of coal which are not sharply divided but overlap because the starting material is similar for all coals. In order of increasing rank, coals are classified as lignitic, subbituminous, bituminous, and anthracitic. Coal, like wood and peat, contains carbon, hydrogen, oxygen, nitrogen, sulfur, and other elements in small quantities.

The United States has one-third of the world reserve of coal. Nearly 80 percent of the reserve, on the basis of heating value per pound, is bituminous and subbituminous. These ranks of coal are widely distributed over the United States.

Coal is extracted from the earth by underground and strip mining. Modern, mechanized mining has achieved higher productivity and efficiency, greater safety for miners, and a minimum of hard labor. After mining, coal is mechanically prepared to remove impurities and crushed to sizes suitable for its ultimate use. It may be burned domestically or used to generate power, gasified for industrial or home uses, or coked for metallurgical purposes. The by-products from coking—gas, tar, and light oils—can be used as such or processed further to serve as raw materials for the chemical industry.

The bituminous coal and lignite industry, widely dispersed over the Nation, reached its peak production of over 630 million tons in 1947. Between that time and 1963, production dropped 172 million tons per year, the number of mines decreased from 8,700 to 7,940, and the number of men employed dropped from more than 440,000 (in 1948) to 142,000. The decline in production has resulted primarily from the competition of oil and natural gas in the energy market. As a result of our steadily growing population and increasing demands for the thermal generation of electric power, however, there are great expectations for substantially increased coal production in the future, although the buildup probably will be on a gradual basis as competition from oil and natural gas continues and that from nuclear energy for power generation increases. Also, as a result of technological research, it is expected that important new uses for coal will be developed, including the conversion to liquid and gaseous fuels.

BACKGROUND

Coal is the primary energy source upon which the Nation's phenomenal industrial and economic growth has been based. The coal industry grew rapidly and steadily from its early beginning, and reached the 100 million ton production level in the 1880's.

At the turn of the century, there were over 3,000 bituminous coal and lignite mines, employing over 300,000 workers in widely dispersed areas of the country. Production exceeded 212 million tons and was valued at $221 million. In 1918, when bituminous coal accounted for 70 percent of the Nation's total energy production, output reached a peak of 579 million tons. Employment reached 705,000 in 1923, with over 9,000 mines in operation. Following the low levels of production during the depression of the 1930's (when output plummeted to only 310 million tons in 1932 and the number of mines dropped to 5,400), and after more than a decade of operating at a deficit, the industry produced its alltime record of 631 million tons in the postwar reconversion year of 1947, with only 419,000 workers. Ap-

proximately 43 million tons, however, was for overseas export (at that time an abnormal market for coal), primarily to assist in the rehabilitation of Europe. This increase in coal production was indicative of the new and tremendous need for energy. For, although total coal production had increased, its actual share of the energy market declined, with oil and natural gas supplying ever-increasing quantities of fuel to the Nation's expanding energy market.

By 1942 coal contributed 52 percent to total energy production. By 1958 coal's share had declined further and was only 28 percent. Since the peak year of 1947, production has been sporadic. Output was only 392 million tons in 1954, 500 million tons in 1956, 410 million tons in 1958, and 459 million tons in 1963. For the past decade the total value of coal produced has averaged over $2 billion annually. The average value per ton of bituminous coal reached its highest level of $5.08 in 1957; for the 6 years since, average value declined each year and in 1963 amounted to $4.39 per ton, an average yearly decline of 11.5 cents per ton, notwithstanding substantial and continuing increases in wages and in costs of material and supplies. The ability of the coal industry to avert spiraling prices and in some cases actually to decrease prices, so as to hold much of its energy market, has been due to its phenomenal record of increased productivity and efficiency of operation resulting from mechanization, which also has contributed substantially to the drop in employment in the industry. Productivity climbed from 5 tons per man per day in 1930 to 11 tons in 1958 and to nearly 16 tons in 1963, as mechanical loading increased from 10 percent of underground production to 86 percent in 1960, and surface or strip mining increased from 4 percent to 31 percent in the same period. Productivity in the bituminous coal industry of the United States is approximately eight times that of the other coal mining nations of the world.

Coal's decline in some markets has been rapid and drastic. The railroad locomotive fuel market has swung to diesel oil, with coal supplies dropping from 132 million tons in 1944 to only about 1.5 million tons in 1963. There also have been significant declines in retail deliveries of bituminous coal and lignite to other than the leading consuming groups and in shipments to miscellaneous manufacturing and mining industries.

While the annual market for coking coal for the iron and steel industry has been declining—averaging 104 million tons per year during the 5-year period ending 1957 and 77 million tons per year during the 5-year period ending 1963—and is expected to continue around the lower level, the brightest spot for coal has been the tremendous demand for steam generation of electricity to meet the phenomenally increasing requirements for electric power throughout the Nation. Bituminous coal and lignite consumption at electric-power utilities increased from 27 million tons in 1933 to 209 million tons in 1963. The upward trend in coal demand by electric power utilities is expected to continue at such an accelerated rate that some estimates of coal requirements for this purpose within the next 15 years range close to 800 million tons per year—more than three times the amount of coal used now.

Because its great bulk requires heavy transportation equipment and facilities, coal historically has been of great importance to the heavy transportation industries. As a result, much of the economic health of these industries, particularly the railroads and, to a substantial degree, water and truck shippers, depends on coal. The economic position of manufacturers of machinery used in mining also is closely allied to trends in the coal industry. In addition, hundreds of communities throughout the country are wholly or substantially dependent on coal mining activity for their economic well-being. The shifting pattern of energy availabilities and consumption in the United States, and the extent to which coal will approach its earlier significance in the energy market, are of critical interest to these components of the Nation's economy, as well as to the coal industry.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF INDUSTRY

The bituminous coal industry ranks high among the major mining industries of the United States in capital value, in value of annual output, and in number of employees. Moreover, production is well distributed throughout the country from the Appalachian region to the Rocky Mountains. In 1963 the value of bituminous coal and lignite production, f.o.b. mines, amounted to over $2 billion. Nearly 8,000 mines employed more than 141,000 men directly in production.

The organization of the industry follows the familiar lines of private enterprise, being highly competitive, with the largest single producer accounting for less than 9 percent of total production. In number, the industry is comprised principally of single-mine producing companies. Larger companies, however, operate several mines, and there is a growing trend toward consolidation in order to effect greater economies of operation and administration. These larger organizations represent the major proportion of production; in 1963, only 9 per-

cent of the mines accounted for 78 percent of total coal production. A sizable portion of total production, 14 percent in 1963, is by "captive" mines, most of which are affiliated with the steel industry and a much smaller portion with the electric utility industry.

A national trade association for the industry, many local associations, an export association, and several producers' associations for wage bargaining purposes exist. Except in the field of safety, in times of national defense emergencies, and in the possible application of such measures as the Taft-Hartley Act and the Sherman antitrust laws, there is no direct Government control of the industry in the sense of regulated production, marketing, or prices as exists in some coal-producing countries.

Over the years there have been wide variations in production in the several States. For instance, total production in the United States reached its peak in 1947 (see table 1). Maryland, Arkansas, and Michigan all reached their maximum production in 1907. Nine States including Illinois and Pennsylvania, reached their peak during World War I. In contrast, Kentucky, West Virginia, and Utah attained their maximum output in 1947, and Virginia was largest in 1963. Ranked in terms of production in 1963, West Virginia was first followed by Kentucky, Pennsylvania, and Illinois, in the order listed. Only six States have produced over 1 billion tons from earliest records to the end of 1963: Pennsylvania (8.5 billion), West Virginia (6.8), Illinois (3.8), Kentucky (2.9), Ohio (2.2), and Indiana (1.2).

There are wide differences among regions in production, number of mines, uses of coal, average value per ton, men working, days worked, and output per man-day. Most of these differences are explainable in such terms as extent of mechanization, quality of product transportation, and market demands.

TABLE 1.—*Maximum and total production of bituminous coal and lignite in the United States by States*

[Thousand short tons]

State	Maximum production		Total production from earliest record to end of 1963
	Year	Quantity	
Alabama	1926	21,001	997,799
Arkansas	1907	2,670	99,539
Colorado	1917	12,483	520,867
Illinois	1918	89,291	3,797,396
Indiana	1918	30,679	1,210,616
Iowa	1917	8,966	355,845
Kansas	1918	7,562	282,859
Kentucky	1947	84,241	2,921,184
Maryland	1907	5,533	269,699
Missouri	1917	5,671	298,291
Montana	1944	4,844	172,127
New Mexico	1918	4,023	128,437
North Dakota	1950	3,261	[1] 103,500
Ohio	1920	45,878	2,194,711
Oklahoma	1920	4,849	183,903
Pennsylvania	1918	178,551	8,493,723
Tennessee	1956	8,848	412,623
Utah	1947	7,429	276,684
Virginia	1963	30,531	906,122
Washington	1918	4,082	149,114
West Virginia	1947	176,157	6,835,126
Wyoming	1945	9,847	411,852
Other States [2]			188,052
United States	1947	630,624	31,210,069

[1] Excludes production in 1954 to avoid disclosing individual company confidential data. Included in other States.
[2] Includes Alaska, Arizona, California, Georgia, Idaho, Michigan, North Carolina, Oregon, South Dakota, Texas, and North Dakota in 1954 only.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Classifications of coal are based on their nature and chemical composition, and these in turn depend on the kind of original plant material, its partial decay in peat swamps, and subsequent metamorphism by geological processes throughout the ages. Various national classification systems have been developed to describe the characteristics of domestic coals. Although many of these systems had features in common, the different terms and standards used to describe similar or identical coals have caused confusion in evaluating coals shipped in international trade. In 1949 the Coal Committee of the Economic Committee of the Economic Commission for Europe established a Classification Working Party to develop an international system for classifying coal. Every major European coal producing or consuming country and the United States participated in this work, which resulted in developing a system for the international classification of hard coals by type and beginning work to develop a similar system for lower rank coals.

Coal, like wood and peat, contains carbon, hydrogen, oxygen, nitrogen, sulfur, and other elements in small quantities. The proportions in which the major elements are present differ greatly in different kinds of coal, and the chemistry of coal is quite complicated. For practical purposes, however, coal is analyzed by proximate analysis or sometimes by a more complete test—ultimate analysis—to determine the amounts of chemical elements.

The *proximate analysis* of coal involves the determination of four constituents: (1) water, called moisture; (2) mineral impurity, called ash, left when the coal is completely burned; (3) volatile matter, consisting of gases or vapors driven out when coal is heated to certain temperatures; and (4) fixed carbon, the solid or cokelike residue that burns at higher temperatures after volatile matter has been driven off. *Ultimate analysis* involves the determination of carbon and hydrogen as found in the gaseous products of combustion, the determination of sulfur, nitrogen, and ash in the material as a

whole, and the estimation of oxygen by difference.

Moisture, sulfur, and ash are the undesirable ingredients of coal. Volatile matter and fixed carbon are the most important contributors to the energy produced when coal is burned; and producing energy in the form of heat is the largest use of coal.

To find the heating value of a particular coal, a sample is weighed precisely and burned in a calorimeter, i.e., a bomb filled with compressed oxygen and immersed in a measured quantity of water at a known temperature. The heat released during the combustion of the coal sample is transferred to the calorimeter, and the rise in temperature is observed. The heating value of coal is then calculated, and is generally expressed in British thermal units (Btu) per pound. One Btu is the amount of heat needed to raise the temperature of 1 pound of water 1° F.

The rank or degree of coalification of the higher rank coals depends on the amount of fixed carbon in the coal, as indicated by proximate analysis. For the lower rank coals, heating value and caking and weathering properties are used to define rank. The rank of coal increases as the amount of fixed carbon increases and the amount of moisture and volatile matter decrease. There is great variation in the composition of coals, as can be seen from the following analyses, on an ash-free basis, of a typical lignite, the lowest rank of coal, and an anthracite, the highest:

	Lignite (percent)	*Anthracite (percent)*
Fixed carbon	33	92
Volatile matter	26	5
Moisture	41	3
Total	100	100

Table 2 lists the ranks of coal; a general description of these coals is given below. *Lignite* (including brown coal) ranges in appearance from brown to black. It yields a brown powder when ground or when rubbed over a rough, white surface. American lignite as mined contains 30 to 45 percent moisture. When exposed to air it loses moisture and crumbles to slack. Although there are large deposits of lignite in the United States, its production is not yet important nationally, partly because it is far from major markets. Greater precautions must be taken to store it satisfactorily, and its heating value is lower than bituminous coal, making the shipment of unprocessed lignite for long distances uneconomic.

Subbituminous coal is black; as mined, it looks much like the bituminous coal commonly seen in coal yards. It contains 15 to 30 percent moisture. The range of heating values of subbituminous A coal is the same as that of high-volatile C bituminous coal. Subbituminous coal is entirely noncoking. Like lignite, it weathers upon exposure to air and is more difficult to store than are the higher rank coals, and it is used principally in the areas where it is mined.

Bituminous coal is the most abundant and widespread rank of coal in the United States. It is the coal used most commonly for industrial, power, and space-heating purposes. Bituminous coal may be either coking or noncoking. This property is not based on the rank of the coal but rather on whether it will produce a coke when processed in a coke oven. Nearly all eastern bituminous coals have caking properties, but many of the western bituminous coals are noncoking and are free burning.

Both *coking* and *caking coals* soften and flow when they become almost hot enough to take fire. As they are heated further, some degradation occurs, and volatile matter escapes as gas and vapors. When coking coals are heated red hot in a sealed oven where there is little or no air, a dull gray, porous mass—coke—remains after most volatile liquids and gases have been driven off. Because coke consists largely of fixed carbon, coking is often called carbonization. Under similar conditions, caking coals agglomerate, yielding a product not acceptable for coke from a strength standpoint.

Noncoking bituminous coal may look like coking coal, and its composition may be similar, but it burns freely without pronounced agglomeration. Instead of a porous mass, it leaves a char of powdery residue. Noncoking and coking bituminous coals may be used interchangeably as a fuel for power plants, railroads, and heating and cooking. For some purposes, however, coking coals are required, the principal one being the manufacture of coke for smelting iron ore in blast furnaces. Noncoking coals are used for cement and tile manufacture.

Most bituminous coals appear black and lustrous in the pile; but close inspection shows a banded structure with alternate layers of bright, glossy coal and dull, grayish black coal. In some coals this dull material predominates, and these are known in the trade as *splint coals*. In thin sections, red and yellow areas representing different constituents can be observed. Finely powdered coal generally appears brown.

Anthracite, sometimes called *hard coal*, usually has a brilliant luster and uniform texture. Anthracite has a higher percentage of fixed carbon and a lower percentage of volatile matter than the lower rank coals. It burns slowly, with a pale-blue flame free from smoke. Most anthracite has a somewhat lower heating value than the highest grade bituminous coals, but its lack of soot and the fact that it will burn

TABLE 2.—*A.S.T.M. classification of coals by rank*[1]

[F.C.=fixed carbon; V.M.=volatile matter; Btu=British thermal units]

Class	Group	Limits of fixed carbon or Btu, mineral-matter-free basis	Requisite physical properties
I. Anthracitic	1. Meta-anthracite	Dry F.C., 98 percent or more (dry V.M., 2 percent or less).	Nonagglomerating.[2]
	2. Anthracite	Dry F.C., 92 percent or more and less than 98 percent (dry V.M., 8 percent or less and more than 2 percent).	
	3. Semianthracite	Dry F.C., 86 percent or more and less than 92 percent (dry V.M., 14 percent or less and more than 8 percent).	
II. Bituminous[3]	1. Low-volatile bituminous coal	Dry F.C., 78 percent or more and less than 86 percent (dry V.M., 22 percent or less and more than 14 percent).	
	2. Medium-volatile bituminous coal.	Dry F.C., 69 percent or more and less than 78 percent (dry V.M., 31 percent or less and more than 22 percent).	
	3. High-volatile A bituminous coal.	Dry F.C., less than 69 percent (dry V.M., more than 31 percent); and moist Btu,[4] 14,000[5] or more.	
	4. High-volatile B bituminous coal.	Moist Btu,[4] 13,000 or more and less than 14,000.[5]	
	5. High-volatile C bituminous coal.	Moist Btu,[4] 11,000 or more and less than 13,000.[5]	Either agglomerating or nonweathering.[6]
III. Subbituminous	1. Subbituminous A coal	----do----	Both weathering and nonagglomerating.
	2. Subbituminous B coal	Moist Btu,[4] 9,500 or more and less than 11,000.[5]	
	3. Subbituminous C coal	Moist Btu,[4] 8,300 or more and less than 9,500.[5]	
IV. Lignitic	1. Lignite	Moist Btu,[4] less than 8,300[5]	Consolidated.
	2. Brown coal	----do----	Unconsolidated.

[1] This classification does not include a few coals that have unusual physical and chemical properties and that come within the limits of fixed carbon or Btu of the high-volatile bituminous and subbituminous ranks. All of these coals either contain less than 48 percent dry, mineral-matter-free fixed carbon or have more than 15,500 moist, mineral-matter-free Btu.

[2] If agglomerating, classify in low-volatile group of the bituminous class.

[3] It is recognized that there may be noncaking varieties in each group of the bituminous class.

[4] Moist Btu refers to coal containing its natural bed moisture but not including visible water on the surface of the coal.

[5] Coals having 69 percent or more fixed carbon on the dry, mineral-matter-free basis shall be classified according to fixed carbon regardless of Btu.

[6] There are three varieties of coal in the high-volatile C bituminous group, namely (1) agglomerating and nonweathering; (2) agglomerating and weathering; (3) nonagglomerating and nonweathering.

longer without attention make anthracite a more desirable domestic fuel than bituminous coal.

There are four types of bituminous and subbituminous coal—common-banded, splint, cannel, and boghead.

Common-banded coal includes most of the coals. It is composed of both anthraxylon (bright bands) and attritus (dull bands) in varying proportions and has a bright luster. *Anthraxylon*, meaning "coal from wood," is the name given to the glossy, jet-black bands in a lump of coal. These bands were formed from the woody parts of plants—their stems or trunks, limbs, and branches. *Attritus* refers to the finely divided matter of which the dull bands of coal are largely composed. This material is a mixture of plant debris consisting of the more resistant residues of various parts and organs of plants, such as cell walls, leaf tissue, spore coatings, pollen, and resin particles.

Splint coals are composed almost wholly of attritus, with only a little anthraxylon. The coal is dull, grayish black, hard, and tough. When mined, it breaks into block lumps; because of this characteristic, it is called *block coal* in some mining regions. Splint coal is good fuel for steam power plants. The name splint coal is probably derived from the fact that large lumps splinter on heating. Used in blends with banded coals, it may improve coke structure.

Cannel coals are also made up almost entirely of attritus. They are often rich in spores, the reproductive organs of the lower plants that do not produce seeds. This coal usually contains a high percentage of volatile matter and burns with a long, yellow flame. It used to be called *candle coal* because of the appearance of the flame and because it can often be lighted with a match. Cannel coal differs from splint coal in that it is more easily ignited, and retains its shape in burning. Cannel coal is used chiefly as a fireplace fuel; it was a desirable coal for making illuminating gas in an earlier era. It usually occurs in small lenses or deposits in beds of other coals and may be separated from them during mining.

Boghead coal is a variety of bituminous or subbituminous coal that looks and burns much like cannel coal. It is made up largely of the remains of algae—water plants that form the greenish or brownish scum often seen on freshwater ponds and reservoirs in summer and fall. It is rich in volatile matter. When distilled, it yields a great deal of gas, tar, and oil. Like cannel coal, it is usually found in small deposits or lenses.

TECHNOLOGY

Coal has been used for more than 2,000 years. As a result of technologic achievements both within and outside of the coal industry, and the steadily increasing demands for fuel, coal has found new markets, and new applications. These, in turn, have required the development of new or improved technology in mining and preparation. During the last 20 years, mining has been mechanized to an increasing extent,

and preparation techniques are being modified to solve the problems associated with mechanization, and with changing patterns of utilization. These aspects are discussed in greater detail below.

Geology

Although coal is commonly thought of as a mineral, it differs from the broad definition of minerals that are natural inorganic elements or compounds, having a definite chemical composition. Coal is of organic origin, formed from the remains of living things—aquatic and land plants including trees, shrubs, herbs, vines, and ferns—that grew millions of years ago, during periods of tropical or mild, humid climates. Some types of plants appear to have contributed more importantly than others to the original deposits. The physical and chemical changes which the vegetation underwent are primarily responsible for the type of coal produced. Many of the plant forms found in coals that are more than 200 million years old are similar to species commonly known today.

The heavy growth of trees, ferns, and other plants in swamps and bogs that grew and fell century after century, accumulating in situ, was buried to a gradually increasing depth each year by new accumulations. These plant remains changed gradually to peat, just as decaying vegetable matter is doing today in the Dismal Swamp of Virginia and North Carolina and in smaller swamps and bogs in many areas.

Peat is the first product when organic matter begins to change to coal. In a block of peat one can often see, with the naked eye, woody fragments of stems, roots, and bark. As peat is buried, it is cut off from the oxygen in air, and rapid decay of its organic matter is prevented by slowing bacterial action. The weight of more vegetation falling on the peat helps to compress and solidify it, as does the weight of water when the deposit sinks below a lake or sea, as has often happened. Sometimes mineral sediments have settled from muddy flood waters while vegetable matter was accumulating and formed partings or layers of shale in the resultant coal bed. At the end of coal-forming periods, swamps remained flooded for a long time, and earthy sediments were deposited in thick beds over the peat, further compressing it and starting coalification, the coalmaking process.

Coalification is extremely slow when it depends mainly upon pressure generated by overlying rock. For this reason, many coal deposits are still of low rank, that is, in an early stage of coalification, although they have been buried millions of years. A few deposits, however, are situated where profound movements of the earth's crust occurred during periods of mountain building. This rock movement generated heat, pressure, and shearing forces producing high-rank coals, such as medium- and low-volatile bituminous coal and anthracite.

The coalfields of the United States cover roughly 400,000 square miles or approximately one-ninth of the total area of the United States. According to the latest estimate, the total recoverable reserves of coal are 1,735 times the 1963 annual production (on a ton-for-ton basis and 1,380 times on a Btu basis). The distribution of these reserves and other related information are discussed in later sections of this chapter.

Mining

In America, coal first was recovered from coal outcrops on the hill and mountain slopes with picks and shovels and simple methods of conveying. However, as the more accessible outcrops were depleted, it was necessary to follow the coal measures into the earth. The coal mining industry then was faced with new and complex problems such as ample transportation facilities, mine ventilation, and roof control. Solving these problems became the primary objective of improving coal mining technology. Today, these objectives have become: (1) high productivity in terms of tons per man-shift, (2) maximum safety for the miners and (3) minimum need for hard labor.

Methods for obtaining safety in mining have undergone much study and development in recent years. The early method of blasting coal with black powder has been replaced with safer explosives—permissible explosives which have a shorter flame duration. Also, some mines now use compressed carbon dioxide or air for breaking the coal rather than explosives. To prevent a mine roof from caving, props made of wood or steel and yielding steel arches may be used. In the last 12 years the practice of roof bolting has grown phenomenally. Expansion bolts are wedged into holes drilled in the roof to bond the overlying rock and slate strata together thus forming a strong span.

Ventilation in underground mining must be provided, not only to supply fresh air to the worker but to remove explosive gases such as methane trapped in the coalbed and released during mining. Methane concentration must be checked at frequent intervals and, when necessary, ventilation must be increased or men withdrawn from the mine until the explosive danger has been removed. Another hazard of

equal importance is introduced by coal dust, which may form a highly explosive mixture with air. Frequent removal of such dust, washing it down with water spray, and diluting it with nonflammable rock dust help to solve this problem.

Constant vigilance and inspection, testing of equipment for use underground, and adoption of improved practices have greatly lowered the number of accidents in mines. The Bureau of Mines program of training mine inspectors and certifying explosives, shot-firing units, blasting devices, safety lamps, and electrical equipment has contributed greatly to increasing safety in underground mines.

Strip Mining

When coal occurs near the surface, strip or open-pit mining may be more economical. Where the coal deposit is thick, as at Kemmerer, Wyo., the open pit may be terraced down, as in the mining of massive copper ore bodies. In flat country, where the deposit is nearly horizontal and of normal thickness, the earthy cover (overburden) is removed with huge power shovels. The coal is then scooped up by smaller power shovels and loaded into trucks. Operations may follow the bed until the ratio of overburden to coal makes production uneconomic. Another form of strip mining—contour stripping—is used in hilly or rugged terrain where the outcrop runs around the hill or mountain. Again, cost factors determine the depth of cut and width of the strip.

The phenomenal growth of strip mining was made possible by developing large capacity shovels, trucks, and new explosives, such as ammonium nitrate, which is now very widely used for breaking overburden. Some shovels now are 140 cubic yards in bucket capacity. The earlier types of shovels (semicircular serving railroad-type shovels) were replaced by full-revolving shovels able to dig and dump in any direction. In turn, came crawler traction and development of large dragline excavators and Carryall scrapers. Steam and gasoline shovels have been decreasing while electric- and diesel-powered shovels have been increasing. Improvements have been made in power drills for shooting holes in overburden and in trucks for hauling the coal from strip pits to tipples or railroad ramps. Some of the trucks used are now 55 cubic yards in capacity.

Strip mining has a substantial advantage over underground mining: Output per man-shift in strip mines is more than twice as large as in underground mines, resulting in a lower cost and price per ton of strip coal. In 1963, the average value at the mine for underground coal was $4.82 per ton and for strip coal $3.57.

Auger Mining

One of the recent developments in soft-coal recovery is auger mining. Many strip mines, particularly in the rough terrain of the Appalachian region, gradually encounter overburden so thick that continued stripping becomes economically impracticable. These strip mines have vast areas of coal seams exposed along what is known as highwall. Auger mining employs a large auger as a cutting head and a tube and screw for transporting coal. The mechanism is unitized so that the coal-removing system is extensible as the cutter penetrates the coal measure. The auger is generally operated from an outcrop location. The labor force is small, and recoveries of about 60 to 65 percent of the coal are reported. After much experimentation, huge augers were designed to bore horizontally into the exposed solid seam of coal much as a carpenter's auger bores into wood. These augers, 16 to 52 inches in diameter, are mounted on movable frames and bore holes 100- to over 200-feet deep. The coal falls from the auger into a conveyor and is elevated into a truck. This type of mining is generally known as highwall auger mining.

Punch mining, another secondary method of recovering coal which would otherwise be lost, involves the use of either continuous or conventional types of mining equipment. In this type of mining, which follows regular underground and strip mining operations, coal is recovered by the application of underground mining techniques, e.g., the driving of short entries and rooms and recovering the small pillars on retreat. The mined coal is then transported by trucks and other equipment that are normally used in stripping operations.

Auger mining at soft-coal mines in the United States averaged 39 tons per man-day in 1963 compared with 29 tons at strip mines and 13 tons at underground mines. Under favorable operating conditions exceptionally high production is achieved, some mines averaging over 50 tons per man-day.

Underground Mining

Underground coal mines may be directly accessible by slope, drift, or vertical shafts (shaft mines). These terms derive from the manner of entry and of moving coal to the surface. Mining methods include room-and-pillar and longwall mining.

The prevailing mining system in the United States is the traditional room-and-pillar. In general, the entries into the coal measure serve as haulageways and fan out into the coalbed with side or cross entries from which the coal is removed to form rooms. Up to about 50 per-

cent of the coal is left to support the roof—usually slate or rock. To conserve resources and obtain maximum coal output, pillars are sometimes removed on the retreat.

For many years coal was drilled, blasted, and then manually loaded into cars for transportation to the tipple at the surface. Later, cutting machines were introduced for undercutting, overcutting, or making vertical cuts. Lateral cuts were often made for bench mining or keeping partings of slate separate from the coal.

In recent years coal mining has been highly mechanized, and loading and conveying are no longer manual. In fact, continuous mining machines have been developed that cut, load, and convey the coal to belt conveyors for transport to the outside. With the development of mechanization, the use of explosives has declined, and productivity has increased.

One type of continuous miner, mounted on rubber tires or crawler treads, has multiple cutters on a horizontal boom that make vertical cuts from floor to roof. Coal is mechanically swept to a chain conveyor and passed to the rear of the machine onto a shuttle car or a continuous conveyor.

Another type of continuous miner has several circular cutters that revolve vertically. The cuttings are thrown, by appropriate opposed directions of rotation (clockwise and counterclockwise) of the cutters, to the center of the machine front and are carried back on an integral conveyor.

These machines represent typical, fully mechanized machines used in room-and-pillar and modified room-and-pillar mining in the United States.

A coal planer or plow, designed for longwall mining, consists of a heavy base that extends the full length of the working face (300 to 600 feet long) and contains a coal conveyor. The plow is on the side of the base that faces the coal. It holds several cutter bits in a guide that point in opposite directions parallel to the coal face. In the guide is the pulling chain powered by electric motors at the extreme ends of the base. When power is applied, the planer rips off a thickness of about 4 inches of coal at the rate of 75 feet a minute. Coal falls onto the conveyor and is spilled continuously at the end of the machine onto other transporting systems. The long base is automatically kept tight against the face by air-operated piston jacks. Roof control in this case is temporary and effected by yielding props (50 tons per square inch) and collapsible cribs. The props are manually leapfrogged toward the receding working face. Behind the props the roof is allowed to break and fall. Because of the creation of voids, the broken roof occupies almost the same volume that it had originally plus that which the coal occupied, so that disturbance at the surface is small. The production of the coal planer is high.

A much simplified picture of coal-mine mechanization has been presented. Developments along that line, particularly rapid in the last decade, are still proceeding. Even today, although many mines are only partly mechanized, about five-sixths or more of all coal mined is mechanically loaded.

The first major task in underground mining—undercutting of the coal seam—was the first function to become mechanized, 25 percent having been cut by machines as early as 1900. The percentage in 1963 was 61. Similarly, hand drills have been replaced by power drills, the latter being used in 64 percent of total underground production by 1963. Continuous mining machines accounted for approximately 40 percent of total coal mechanically loaded underground in 1963. Mechanical loading has already been mentioned. Although some animals, mostly mules, still are used for hauling in small mines, they have been generally replaced by electric locomotives, rope haulage, belt conveyors, or shuttle cars.

Preparation

As a result of the developments in mechanization, the quantity of bituminous coal mechanically cleaned in the United States increased from 28 million tons (5 percent of total production) in 1927 to 289 million tons (63 percent of total production) in 1963.

In the early days of coal production, screening and hand picking of slate and rock at the working face constituted the preparation of coal. As time went on, crushing became an important factor in fitting coal to the needs of consumers. More recently, greater emphasis has been placed on quality of coal and removal of extraneous material. To meet this requirement and sales competition, coal washing or cleaning grew in importance; this operation has been carried out largely by machine. The introduction of mechanized mining, which does not differentiate between coal and impurities has given great impetus to coal preparation. Nearly two-thirds of all coal mined in the United States is now mechanically cleaned.

Cleaning consists of removing high ash bands, rock, ash-forming material, and sulfur-bearing components of coal. Sulfur occurs generally in two forms—inorganic matter such as pyrite (iron sulfide), and organic sulfur compounds that are inherent in the basic coal substance. The latter is not now separable, whereas part of the inorganic sulfur is separable.

Separation of impurities from coal is based primarily on differences in density, the sep-

arable impurities being heavier than an equal volume of coal. The natural force of gravity is employed in addition to forces such as centrifugal force and those introduced by agitation, jigging, flow of water, and the like. Differences in density are utilized by separation in air, water, chemical solutions, suspensions, or slurries, and air flotation with special wetting agents.

Coal-Cleaning Systems

The most popular system for cleaning coal in the United States is the use of jigs. In this unit, the raw coal feed is stratified in water into a series of layers of different density by mechanical impulses applied to the water. Other systems use the flow of water to achieve cleaning. In the cleaning of fine coal, the coal washing table utilizing a flow of water combined with a differential movement of the table itself is used widely in this country.

In the dense-medium processes, coal is separated from its associated impurities by suspension of finely divided solids in water, aqueous solutions of inorganic salts, and organic liquids. Magnetite, pulverized, refuse, loess, sand, and barites are frequently used as suspended solids in the process. Calcium chloride solutions are the predominant means of cleaning coal using soluble inorganic salts. In this process, the separating medium is adjusted to achieve a predetermined gravity of separation, permitting the clean coal to float and the heavier refuse materials to sink in the bath.

For the cleaning of very fine sizes of coal, flotation procedures must be employed. In these, the mixture of coal and impurities is fed into a water bath, flotation agents are added, and the bath is aerated with small bubbles of air. The flotation agent (such as kerosine plus pine oil) wets only the coal particles, which are attached to air bubbles, lifted to the surface of the water, and skimmed off mechanically.

Centrifugal force is employed, in addition to gravity, in the Humphrey spiral, in which the coal to be cleaned and water are passed down a spiral trough. This combination of forces has taken another form in the cyclone separator and thickener, in which the principle of the cyclone is employed as in dust, sawdust, and grain collectors with pneumatic systems.

In other systems, air flows counter to the pull of gravity and separates coal and impurities. Again, suitable takeoffs are provided. This process is known as elutriation when applied to dusts and other fine materials for classification or segregation purposes; when used with coal it is known as air cleaning. A combination of moving air and sand, often in a cone-shaped vessel, is widely used.

Processes have also been developed for drying, removal of dust, addition of calcium chloride to prevent freezing, and surface oiling for cleanliness.

Crushing

The crushing of large lumps into smaller ones permits easier handling and cleaning and meeting market requirements. Before about 1930 the largest sizes were at a premium, and mechanical cleaning was little used. The only reason for crushing, therefore, was to reduce large lumps so that they would pass through the tipple. In subsequent years, however, crushing became essential to meet the customer demand for smaller sizes for use in mechanical stokers, as well as for mechanical cleaning.

Treatment for Allaying Dust

Although dust on coal may be negligible in comparison with the total weight, it creates a nuisance or even a hazard from explosion. Much experimentation has been carried on to develop surface processes for allaying coal dust (as distinguished from dust problems in underground coal mines). Such treatment also tends to prevent freezing of wet coal, reduces windage to prevent freezing of wet coal, reduces windage loss of fines in transit, improves burning performance at times, reduces the tendency toward spontaneous heating during storage, and reduces air slacking and distintegration.

The materials used for such surface treatment are (1) water in conjunction with wetting agents (organic chemical compounds that cause water to spread into a thin film and wet the coal surface readily), (2) calcium chloride with or without various admixtures, and (3) oil or other petroleum products. The predominant treating agent has been oil, except during World War II, when its use was restricted.

Combustion

Most of the bituminous coal produced in the United States is burned in boilers or furnaces to obtain thermal energy for generating electricity, processing raw and manufactured materials, and providing comfort heating in industrial and commercial establishments, institutions, and homes. The electric utility industry is the largest consumer of bituminous coal, accounting for 51 percent of consumption in the United States in 1963. A significant amount of coal is consumed annually for calcining to make cement, lime, gypsum, alumina, and magnesia, and for firing ceramic products. The use of bituminous coal for residential heating and for rail-motive power has declined in

recent years in favor of petroleum and natural gas, but these markets may be partly recaptured within the next 10 years if research investigations now in progress result in feasible and economic processes for converting coal to methane, and in a coal-fired gas-turbine locomotive having a comparatively high degree of availability.

Broadly speaking, combustion is accomplished conventionally by burning coal on a grate, in suspension, or by combinations of these methods.

Basically, a grate is a device on which a bed of coal is ignited and burned in place. Grates may be horizontal or inclined, fixed or movable, vibrating or modulating, but each kind is designed to allow air for combustion to pass through the bed of coal, and to permit removal of ash and clinker. The coal may be charged to the grate batchwise by manual means, or more or less continuously by a mechanical stoker. Grates for residential-heating furnaces are comparatively simple devices, whether they are fired manually or with a mechanical stoker. Grate-stoker combinations for commercial and industrial use are designated as single-retort, multiple-retort, chain, traveling, and spreader stokers. The latter type combines the features of combustion on a grate and in suspension.

For suspension burning, two methods are employed. The coal is pulverized and blown into the combustion chamber with approximately 10 percent of the combustion air, the remainder of the air being supplied as secondary air to complete combustion in the furnace. The ash is removed dry or as molten slag, depending upon the design of the furnace. In the so-called dry-bottom furnace approximately 50 percent of the ash is carried out of the furnace with the products of combustion. Dust-collecting devices remove from 50 to 98 percent of this gas-borne ash. In wet-bottom furnaces less coal ash is carried out with the products of combustion than in dry-bottom furnaces. The other method involves blowing or mechanically throwing crushed coal into the furnaces, where most of it falls on a dump- or traveling grate. Part of the coal burns in suspension, and combustion is completed on the grate. This method generally is referred to as spreader firing and, as mentioned previously, incorporates the features of both grate and suspension firing. Almost all of the bituminous coal used by the electric utility industry is burned in pulverized-coal-fired furnaces, and much that is burned for industrial purposes is burned by spreader firing. The cyclone furnace, which is growing in importance in the utility and industrial fields, is a form of suspension burning. Crushed coal is blown into a cylindrical furnace, and tangentially admitted secondary air imparts vortex motion to the coal and gases. Part of the coal burns in suspension and the remainder, which is trapped in liquid coal-ash slag on the walls of the furnace, burns before the slag is discharged from the furnace. Cyclone furnaces remove about 90 percent of the coal ash as molten slag.

The choice of the type of firing depends upon a number of factors, chiefly the kind and quality of the coal and the amount of thermal energy desired within a given space for equipment. Generally, suspension burning provides more thermal energy than grate firing per unit volume of furnace. However, the capital investment for grate-stoker furnaces is less than that of pulverized-coal-fired furnaces below a certain capacity and vice versa. At the present time, the electric utility industry, which has boilers that generate over 4 million pounds of steam per hour, is based almost exclusively on the principle of suspension burning. To obtain greater thermal efficiencies, the utility industry is installing steam generators capable of steam temperatures up to 1,200° F and pressures of up to 5,000 pounds per square inch, with capacities up to 6.5 million pounds of steam per hour; these specifications were unheard of 15 years ago.

The trend to larger utility boilers has resulted in improving the steam-electric utilities national average heat rate from 15,700 Btu per kwhr in 1946 to 10,500 Btu per kwhr in 1963, while heat rates for a single plant during that period have shown improvement from the 10,608 Btu per kwhr in 1946 to 8,400 Btu per kwhr or slightly under in 1963. This represents a decrease in coal requirement in power generation to approximately 0.7 pound per kwhr or less at some plants. The national average is 0.86 pound per kwhr.

Carbonization

Coal carbonization, i.e., the destructive distillation of bituminous coal by heating it in the absence of air, is a process by which bituminous coal is converted into coke, gaseous, and liquid products. With the increasing use of coke as metallurgical fuel and of the liquid products for direct commercial uses or as starting materials for the manufacture of chemicals, carbonization has grown into one of the United States' most important industries. Approximately one-fifth of the coal consumed in the United States in 1963 was used for the production of coke and coal chemicals. The production of slot-type and beehive coke in 1963 totaled 54,278,000 tons.

Most of the coke produced is used in blast furnaces, and a comparatively smaller amount is used in foundry cupolas. The principle of smelting iron in the blast furnace has remained virtually unchanged since its first introduction in the early part of the 14th century. Successive

layers of iron ore, limestone, and coke are charged to a tall, refractory-lined steel shaft, and preheated air is admitted under pressure, through tuyeres located near the bottom of the shaft. The preheated air creates a combustion zone, induces partial burning of the fuel, and forms carbon monoxide by reaction with the carbon in the fuel. The carbon monoxide, in turn, reduces the iron oxide ore to metallic iron, but the temperature is not high enough to melt the associated impurities in the ore. These impurities, consisting primarily of aluminum silicates (gangue), are fluxed with the limestone to form a slag, which is fluid at about 2,500° F, well below the 3,000° F temperature in the combustion zone of the furnace. This fluid slag and the molten iron are drawn off periodically through separate taps at the base of the furnace, and the iron is cast (into pigs) or transported hot for further processing.

Charcoal was the original and chief source of fuel used in the blast furnace until the latter part of the 19th century. Coke, although first used in Europe in 1735, did not become an important blast-furnace fuel in the United States until long after the production of beehive coke began in 1841. Slot-type oven coke was first introduced in the United States in 1893, and its metallurgical use increased gradually until, in 1919, it exceeded that of beehive coke; it is now used almost exclusively.

The beehive coke oven is a firebrick chamber, approximately 12 feet in diameter and 7 feet high, with an arched roof, whose inside shape resembles an actual beehive. The ovens, built beside one another with a retaining wall between, extend in long rows, and are usually located near the coal mine. Coal is charged into the oven, which holds about 6 tons of coal, through a hole or trunnel head at the apex of the dome, and is leveled. Coking is started by the heat retained in the walls of the oven from the previous operation, or by heating the oven before charging. Almost immediately after charging, gas is evolved from the coal on the coal surface and in the space above. Air is introduced through a side door to support combustion. Coking proceeds downward, from the top of the coal charge to the floor of the oven. The products of combustion and any unburned gases escape through the charging hole at the top. When coking is complete, the door is opened and the coke is quenched with water and withdrawn from the oven. The beehive process requires the use of high-grade coking coals and a long coking time (2 to 3 full days). The coke produced is hard and dense, and large in size.

Various types of slot ovens have been designed and used to recover valuable chemical products and to obtain coke whose quality can be more carefully controlled. Another favorable factor concerning slot ovens is that coal blends may be used. In the slot-type coke ovens, the coal charge is carbonized without direct contact with the heating gases and the distillation products are recovered completely. Although beehive-oven construction involves a lower capital investment, the value of the chemical products recovered from the slot-type ovens is usually more than enough to offset the greater cost of oven construction, so that gradual replacement of the beehive by the slot-type oven has occurred. In the early development of these ovens, the heat required for carbonization was supplied either in horizontal or vertical flues. Recently, however, the vertical flue oven has found wider acceptance because it is more flexible in allowing the use of different fuel gases.

The slot-type coke oven is a long, narrow, silica-brick chamber, in which the coal is carbonized by heat supplied by the combustion of fuel gas in the flues that are built in the refractory-brick walls separating each of the ovens in the battery. Slot-type coke ovens vary in size and capacity. The small ovens, used in small gas plants, coke approximately 4 tons of coal per charge, while the larger ovens, used primarily for production of metallurgical coke, have a capacity of 20 tons or more. The larger ovens are usually 37 to 45 feet long, 9 to 15 feet high, and between 1 and 2 feet wide. An average sized oven with a width of approximately 1½ feet will hold about 17 tons of coal charged at 50 pounds per cubic foot bulk density. For a normal carbonizing time of 17 hours, the capacity of the oven is about 24 tons of coal per day.

Each oven has three or four charging holes. The coal, usually crushed so that 80 percent will pass through a ⅛-inch screen, is dropped through these holes into the oven and the resulting cone-shaped piles are leveled to permit uniform coking, better product recovery, and to facilitate coke removal through the side door. The manufacture of coke for blast furnace use requires 12 to 18 hours, depending on the oven width and the carbonization temperature, while foundry coke production generally requires 20 to 24 hours. After coking is complete, the oven doors are removed and the coke is discharged and quenched with water sprays.

To prevent deterioration of coke ovens that results from cooling and reheating, coke ovens are not allowed to remain empty for any considerable length of time. If the demand for coke decreases, the volume of fuel gas and the flue temperatures are reduced so that the coking period and, hence, coke oven operation is lengthened. As a result, the coke produced will vary somewhat, depending on the capacity at which the ovens operate. Although there are no absolute criteria for defining coke qualities that will

insure the most satisfactory performance of the blast furnace, uniformity in coke size, structure, and other physical and chemical characteristics are desirable.

The coke must be strong enough to resist excessive breakage during handling and charging into the furnace to support the heavy column of materials at the high temperatures in the passage down the shaft. Chemically, the coke should be low in moisture, volatile matter, sulfur, and ash contents. In turn, coals are selected so that, when carbonized, they will produce cokes having the desired characteristics. A good blast furnace coke, as generally defined in the Eastern States, contains no more than 4 percent moisture or 2 percent volatile matter, nor more than 1 percent sulfur, and about 10 percent ash. The chemical composition of a good coking coal or blend is as follows: 4 percent moisture, with a maximum of 7 percent; between 28 and 35 percent volatile matter; 1.5 percent or less sulfur; and 7.5 percent or less ash.

Approximately 98 percent of the coke produced in the United States, is made in slot ovens, about 2 percent in beehive ovens, and a very small amount by various unconventional processes, such as chain-grate stoker cokers, Disco carbonizers, and Lurgi retorts. The unconventional processes may be classified as low-, medium-, and high-temperature carbonization processes depending on final carbonization temperatures attained. Low-temperature carbonization processes are those in which the final carbonizing temperature does not exceed 700° C. In high-temperature carbonization, the final temperature of the coke usually is above 900° C, and the temperature in the heating flue is still higher. Processes which operate at temperatures between these two figures are designated as medium-temperature carbonization processes.

Considerable research and development work on various low-temperature carbonization processes has been conducted for many years, but few have been economically successful. The basic differences in the various low-temperature carbonization processes are in the methods by which the necessary heat for carbonization is transmitted to the coal. One of the low-temperature carbonization processes that has created considerable interest in the coal-processing industry in recent years has been the application of fluidized solid-fuels techniques. The char from fluidized coking can be used efficiently as a powerplant fuel, but it is also known that the tar is not comparable to high-temperature coal tar, and most of the products that can be made from it by conventional methods are not commercially usable in our chemical industry. This does not preclude the eventual economic utilization of low-temperature coal tar, as research and development in processing methods and new products will, no doubt, open up new markets for low-temperature tar. The Bureau of Mines is active in this field at several of its coal research laboratories.

Other unique unconventional carbonizing processes which are either in commercial- or pilot-plant-stage production are (1) the traveling-grate stoker coker, (2) continuous rotary hearth ovens, and (3) formed coke processes.

About 100,000 tons of chemical coke per year is being made with traveling-grate stoker cokers. This process does not require external heat; coal is carried on moving grates through a horizontal furnace, where required temperatures are generated in the bed by controlling the admission of small amounts of air. The hot coke feeds to a finishing shaft furnace and is quenched at the bottom of the furnace by a recycled gas mixture (nitrogen and carbon dioxide). Heat is recycled to preheat the air used in the first stage.

Pilot operations of a rotary hearth oven in southern Virginia indicate that this process is capable of achieving coking rates about 3.5 times that of conventional-type beehive-coke ovens. Although in principle this process is similar to the traveling-grate stoker coker, the furnace design actually is a long tunnel bent into the form of a circle enclosed in a big shell or cap. Another difference is that the whole bed or solid hearth rotates along with the coal. Coal is fed in at one point and coke comes out after completion of the circle 3 hours later. Operating temperatures of 2,400° F is comparable to standard slot-oven coke practice. A second pilot plant was completed in 1964 in Wyoming to test western coking coals.

Those processes which convert noncoking coal into a carbonaceous fuel suitable for various industrial and metallurgical applications by a combination of carbonization and briquetting steps are called formed coke processes. The most notable one tested thus far in a pilot plant stage in this country is the FMC Process. This is a multistage carbonizing process in which the coal goes through catalyzing, carbonizing, calcining, briquetting, curing, and final carbonizing stages. The final carbonizing temperatures range from 1,500 to 1,700° F, which indicate that it is a high-temperature carbonization process.

In addition to coke, four primary coal-chemical materials—tar, ammonia, light oil, and gas—are recovered at oven-coke plants. Initial cooling upon leaving the carbonizing chamber results in the condensation of the heavier high-boiling constituents comprising coal tar; further cooling with water and scrubbing with sulfuric or phosphoric acid effects the recovery of ammonia either as an aqueous solution or in the form of ammonium sulfate or diammonium

phosphate; still further cooling, followed by oil washing, removes light oils consisting of benzene, toluene, xylene, solvent naphtha, and naphthalene. After this point in the system, only gas remains as the final primary product. Coke-oven gas, which consists mainly as hydrogen and methane, is used mainly as fuel. Only 2 of the 62 active oven-coke plants processed their coke-oven gas for the recovery of hydrogen which in turn was used to manufacture synthetic anhydrous ammonia. This could be changed, however, as new facilities for processing coke-oven gas will be constructed at the largest coke plant in the United States. This company also proposes to build a 400,000-tons-a-year anhydrous ammonia plant to utilize the hydrogen recovered from the coke-oven gas.

Virtually all of the light oil recovered at oven-coke plants is processed by the producing companies. In order to produce light-oil derivatives with purity comparable to similar materials produced from petroleum feedstocks, coke-oven operators are modernizing and constructing new modern refining facilities. Two of the larger coke plants already have installed such facilities, and more can be expected to be constructed in the future.

Gasification

Gasification processes involving the use of coal or coke are used to manufacture gases having specific characteristics, depending on the end uses contemplated. Since reserves of natural gas are limited and may have to be supplemented by gases produced from coal, a great deal of attention has been directed, both in the United States and abroad, to the development of economic processes for such gas production.

Coal can be gasified with steam and air or oxygen, at atmospheric or elevated pressure, to produce synthesis gas (for chemical manufacture, production of hydrogen and synthetic liquid fuel, etc.) and producer gas (for industrial heating). In a two-step process, synthesis gas produced from coal gasification can be catalytically transformed to high-Btu pipeline gas. Coal can also be gasified in place, underground, with air or oxygen, to produce a gas suitable for power generation and other industrial uses.

The underground gasification of coal, explored on an experimental basis in the United States and abroad, is uneconomic under present conditions. This process is, however, being used in the U.S.S.R. for production of gas for power generation.

Synthesis gas, a mixture of carbon monoxide and hydrogen, can be produced by passing air (or oxygen) and steam alternately or continuously through a bed of hot coal or coke. Synthesis gas is now being produced on a commercial scale abroad by passing oxygen and steam continuously through a bed of coal, under pressure, and, in the Sasol plant in South Africa, is being used for the production of liquid fuel. It is also produced by entraining pulverized coal in a stream of oxygen and steam.

Producer gas is made by passing a mixture of air and steam continuously through a hot fuel bed, with the resultant gas being used for industrial process heating.

The catalytic methanation of synthesis gas produces a high-Btu gas, is technically feasible and, when economically practicable, could be used to produce a substitute for natural gas. Research is in progress to improve this process, to permit one-step conversion, at reduced cost.

In addition to the conventional techniques described earlier, the Federal Bureau of Mines in cooperation with the Atomic Energy Commission, is investigating the possibility of using nuclear fission to supply the reaction heat required for the direct gasification of coal with steam to produce increased yields of synthesis gas. Research is now in progress, with current tests involving the use of a simulated nuclear reactor, i.e., an electrically heated reactor.

The coal required and the yields and quality of gas produced in each of the above processes vary greatly, depending on the operating conditions and, in turn, on the end applications contemplated.

Hydrogenation

Hydrogenation of coal at elevated pressures and temperatures is another process for converting this valuable and plentiful solid fuel to other products that have potential value and a large established market, e.g., to synthetic liquid fuels (motor and aviation gasoline, and liquefied petroleum gases), and chemical intermediates or raw materials, and supplements to or substitutes for natural gas.

The liquid-phase hydrogenation of coal was used in Germany during World War II to produce gasoline and oil products. The direct hydrogenation of coal is being investigated in the United States on a laboratory and pilot plant scale and was evaluated in the demonstration plant at Louisiana, Mo. The data obtained from these studies have indicated that, although the process is technically practicable, the costs involved do not permit commercial exploitation of the process under present economic conditions.

Attention has also been directed toward the possibility of hydrogenating coal to produce marketable chemicals or chemical raw materials, such as benzene, toluene, phenols, etc. The type and quantity of products are determined by

the operating conditions. Similar products are obtained from other sources, as byproducts of coal carbonization and petroleum refining, and are currently more economically produced. Hydrogenation of coal to produce gaseous hydrocarbons (equivalent to natural gas) is also under investigation.

USES

Most of the coal produced is burned for heat and power production, or carbonized to produce metallurgical coke. Although there are other uses of coal and potentially important new uses are now being developed, these are of relatively minor importance in terms of large tonnages in the actual and present utilization scheme.

For example, the gasification of coal, which has had an important role in American industry, has undergone many changes. Producer gas, formed by passing limited and controlled quantities of air and steam through ignited coal, found extensive use in industry for operations requiring heat, such as coking and ceramic firing.

Coal, when coked, produces a valuable gas (about 10 to 11,000 cubic feet per ton of coal) of good heating quality (about 550 Btu per cubic foot) with a composition that makes its utilization as raw material for synthetic chemical production feasible. Such utilization is now beginning in the United States. This gas has been used over the years as a domestic gas and for industrial purposes.

Coke has been the source of much water gas, a mixture of mainly hydrogen and carbon monoxide. This gas is produced by the action of steam on incandescent coke and has a heating value of about 300 Btu per cubic foot. For many years, enriched in heating value to 500 to 550 Btu by gases from cracked oil, carbureted water gas has served as domestic gas. As the ratio of hydrogen to carbon monoxide is adjustable by chemical reaction, water gas can provide hydrogen for ammonia synthesis, for hydrogenation of oils to make margarine and cooking fat, and to convert coal to chemicals and liquid fuels. Water gas also serves as raw material for the synthesis of motor fuels, methanol, higher alcohols, and other chemicals.

The advent of natural gas (mainly methane) and its distribution in volume in recent years have caused changes in the production and use of gas from coal in almost all fields, whether its use be as a fuel or as a chemical raw material. Methods are now being studied (and used to some extent abroad) for converting coal to methane.

Most coal produced today is burned to provide energy—to generate electricity, provide process heat, and heat for domestic use. Coal is burned for space heating, whether heat distribution is by warm air, hot water, steam, or electricity. It is burned to supply hot water and steam for many purposes. One of the most important of these numerous uses is the generation of electric power for lighting, manufacture, transportation, communication systems, air conditioning, domestic appliances, and the like. The combustion of coal and its control and application for technical purposes are being intensively studied and developed. In fact, burning of coal has, to a large degree, become a science. Pulverized coal can now be moved and handled like a fluid (analogous to oil and gas). Combustion has developed from simple burning on rudimentary grates, stoves, and furnaces to a highly complex operation, instrumented for efficiency and automatically controlled.

The largest and fastest growing market for coal is the electric utility industry. The technologic advances in coal mining, preparation, and combustion equipment design have combined to increase efficiency of power generation to a point where competitive fuels would require large reductions in price to compete commercially with coal. Although plant efficiencies vary considerably, the 1963 national average for electric utility plant consumption of coal was 0.86 pound of coal per kwhr, with new plants built for operation on approximately 0.7 pound of coal per kwhr. In 1920, 3 pounds of coal was consumed in the United States for 1 kwhr of electricity.

As noted earlier, coal is also burned or used to supply heat for industrial process use, in the manufacture of cement, and other products, with the ratio and quantity of coal used determined by advances in process and equipment design. The ash may be used in the manufacture of rock wool for insulation and in applications described in the "Byproducts and Coproduct" section.

The use of coal for motive power and residential heat has decreased with the advent of petroleum products and natural gas and the more convenient equipment and handling the use of these products entails. Attempts are, however, being made to develop techniques that would permit the coal industry to maintain and to expand its present share of these markets. Although the increasing use of competitive fuels appears inevitable, advances in the technology of coal gasification, the conversion of coal to gaseous and liquid fuels, may afford a new and better opportunity for coal to recover its share of these markets.

The second largest outlet for coal is the steel industry. Approximately one-fifth of the coal consumed in the United States is used for the production of coke for metallurgical use and, as byproducts of the carbonization process, of

coal chemicals. Almost 1½ tons of coal is needed to produce 1 ton of coke which, in turn, is required to make about 1¼ to 1½ tons of pig iron. Bituminous coals having acceptable properties and characteristics are carbonized at high temperatures to produce coal tar and light oils which serve (1) as raw materials for organic chemicals like synthetic rubber, detergents, plastics, photographic materials, flavor and perfume chemicals, explosives, and medicinals, and (2) after comparatively slight processing, as wood preservatives, disinfectants, animal dips, and road and building materials.

Low-temperature carbonization (at 900° to 1,000° F compared with about 2,000° F for high-temperature or coke-oven carbonization) is a little-practiced but promising use of lower rank coals for producing smokeless fuel, industrial carbons, and substantial quantities of low-temperature tar and oils. A prototype unit for the low-temperature carbonization of lignite has been constructed and operated in Texas for the production of a char suitable for use as a boiler fuel. The carbonization of lignite does not result in the production of coke; a char is produced which, on further processing and recarbonization, could be used in some metallurgical applications. The commercial exploitation of this process, however, depends on the realization of a market for the liquid and gaseous products. When economical operation of low-temperature carbonization is achieved, it should result in expansion of coal consumption and the use of large and virtually untapped fuel reserves.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

The production of coal chemicals as byproducts of coke production is established and will not be considered in this section. However, the use of residual products from combustion of coal, i.e., fly ash, flue dust, coal ash and cinders, as well as rejects from the preparation plant, is a possible means for either recovering or producing various chemicals and materials. These products are and may continue to be used increasingly by the building industry in the manufacture of cement and concrete products and for such uses as the construction of roads.

Fly ash is used primarily in the building industry, in the manufacture of concrete, building stones, and cinder blocks, and in asphalt highway construction. Coal cinders have also found application in the manufacture of cinder blocks for the building industry.

Coal furnace flue dust, a commercial source of germanium in England, is not processed commercially in the United States. Germanium and other elements (such as vanadium, lithium, and uranium) also can be recovered from coal ash. Coal ash was used during wartime as a source of alumina, producing 1 ton of alumina from 10 to 12 tons of coal, and this process is now again attracting commercial attention. Lignitic uranium ores of commercial importance have been discovered in North Dakota.

Washery refuse has, in the past, been used as a source of sulfur. Two companies in the United States are now using preparation plant rejects for the production of lightweight aggregates on a commercial scale.

ALTERNATE MATERIALS

Natural gas and petroleum, considered in other chapters, and atomic energy are competitive with coal as sources of energy. Much theoretical and applied research has been pursued that would advance the possibility of developing new and unconventional sources of energy to substitute for the mineral fuels used today. Atomic energy is now a reality and will grow in importance. However, when the exploitation of one or more new sources of energy is contemplated, consideration must be given to the availability of fuels, the character and magnitude of the demand for power, and the anticipated cost of power produced from the new sources. Under these conditions, most estimates indicate that complementary energy sources will not significantly affect the energy market before the 1980–2000 period.

RESERVES

The United States is richly endowed with mineral-fuel resources. It has one-third of the geologically estimated coal and lignite reserve of the world, one-tenth of the proved petroleum reserve, and about one-third of the world's proved natural-gas reserve. The United States also is the greatest producer of solid, liquid, and gaseous mineral fuels as a whole. In 1963 the Nation produced 22 percent of the world production of coal, less than 1 percent of world lignite, 30 percent of all petroleum and 60 percent of the natural gas.

The Federal Geological Survey estimated the remaining coal reserve of the United States, including Alaska, at 1,660 billion tons as of January 1, 1960. The reserve estimates include beds down to 14 inches thick for anthracite and bituminous coal and down to 30 inches or more thick for subbituminous coal and lignite. The reserve is largely geologically inferred, and estimates did not allow for mining losses or recognize that beds less than 2 feet thick are not

economically minable by present underground methods. Investigations by the Bureau of Mines and others have shown that, on the average, about 50 percent of the coal is recovered in underground mining. Losses include coal left in pillars, in areas around oil and gas wells, under towns, railroads, roads, and streams, in river beds, in thin and impure beds, and in isolated areas not readily accessible for mining.

Table 3 lists the recoverable reserves of coal in the United States, as of January 1, 1960. The recoverable total of 830 billion tons represents one-half the total resource and includes 380 billion tons of bituminous, 224 billion tons of lignitic, 218 billion tons of subbituminous, and 8 billion tons of anthracitic coal; however, the average heating values of the several ranks of coal decrease from 14,000 Btu for low-volatile bituminous coal to 6,700 Btu for lignite. Therefore, these coals have also been compared, in terms of energy obtainable from them, by converting the tonnages given in column 1 to equivalent tons of bituminous coal of 13,000 Btu per pound. Thus, a reserve of 224 billion tons of lignite equals 115 billion tons of 13,000-Btu bituminous coal in heating value.

Tables 4 and 5 show the distribution, by rank and geographical location, of these coal reserves on the basis of equivalent heating value. According to this method of evaluation, about 54 percent of the minable reserve of coal and lignite is in the Eastern and Interior provinces and 46 percent in the Northern Great Plains, Rocky Mountain, Gulf, and Pacific provinces.

The Eastern Province consists of Pennsylvania, Ohio, Maryland, West Virginia, Virginia, eastern Kentucky, Tennessee, and Alabama; the Interior Province consisting of Illinois, Indiana, western Kentucky, Iowa, Missouri, Kansas, Oklahoma, and Arkansas; and the northern Great Plains, Gulf, Rocky Mountain, and Pacific Provinces consisting of North Dakota, South Dakota, Montana, Idaho, Wyoming, Colorado, Utah, Arizona, New Mexico, Texas, Washington, Oregon, and California.

TABLE 3.—*Potential recoverable reserves of various ranks of coal as of January 1, 1960*

Rank of coal	Billion short tons (1)	Bituminous coal of 13,000 Btu per pound calorific value, equivalent billion short tons (2)	Total coal reserves on Btu basis, percent (3)	Heating values used in conversion, Btu (4)
Anthracite	8	8	1	12,700
Bituminous	380	395	58	13,500
Subbituminous	218	159	24	9,500
Lignitic	224	115	17	6,700
Total	830	677	100	

TABLE 4.—*Distribution of recoverable coal reserves in terms of Btu value, by ranks and provinces*

[Weight basis]

Rank of coal	Equivalent 13,000 Btu coal, billion short tons				
	Anthracite	Bituminous	Subbituminous	Lignitic	Total
Eastern	6.0	218			224.0
Interior	.1	205			205.1
Northern Great Plains, Rocky Mountain, Gulf, and Pacific	.4	116	136	119	371.4
Total	6.5	539	136	119	800.5

TABLE 5.—*Distribution of recoverable coal reserves in terms of Btu value, by ranks and provinces*

[Percentage basis]

Rank of coal	Anthracite	Bituminous	Subbituminous	Lignitic	Total
Eastern	1	27			28
Interior		26			26
Northern Great Plains, Rocky Mountain, Gulf, and Pacific		14	17	15	46
Total	1	67	17	15	100

Eastern and western coals differ sharply in rank. Virtually all of the Eastern and Interior province coals, except anthracite, are caking bituminous coals. Coals of the Appalachian region are medium to strongly coking, and, in 1963, supplied 93 percent of the coal used for making coke. On the other hand, 70 percent of the coals of the Northern Great Plains, Rocky Mountain, Gulf, and Pacific provinces are subbituminous and lignitic. These coals do not cake on heating.

As a basis for comparison of fuel reserves, committees of the American Petroleum Institute and of the American Gas Association estimated as of December 31, 1963, that the proved United States recoverable reserve of crude oil was 30.97 billion 42-gallon barrels and that of natural-gas liquids was 7.67 billion barrels, making a total of 38.64 billion barrels of liquid hydrocarbons. The American Gas Association committee estimated the proved reserve of natural gas at 276.2 trillion cubic feet; a recent estimate by the Federal Geological Survey of oil equivalent in oil shale deposits in Colorado, Utah, and Wyoming includes 600 billion barrels of oil in shale yielding 25 gallons or more oil per ton.

To satisfy the large and still increasing demand for liquid fuel, more petroleum deposits must be discovered, more petroleum imported, or, from the standpoint of self-sufficiency, syn-

thetic liquid fuels made from natural gas, coal, or oil shale. Each of the procedures probably will be employed to some extent, depending on economic and national defense conditions. Additional domestic reserves of petroleum are being found at a rate almost adequate to supply the increasing domestic demand. Development of oil deposits in South America, Canada, and the Middle East is making oil available for importation to the United States under peacetime conditions and for supplying the growing demand for other countries. Bureau of Mines research at Rifle, Colo., has demonstrated that liquid fuels can be made from oil shale at comparatively small increases over prices prevailing in recent years for corresponding fuels from petroleum. Large reserves of coal and lignite also can be converted to liquid fuels.

Reserves for different mineral fuels are not calculated on the same basis. Proved reserves for liquid and gaseous fuels are increased each year by new discoveries and extensions of fields and decreased by the year's production. More oil and gas reserves will be proved in the United States; in this respect, these fuels differ from coal and oil shale. Solid-fuel reserve estimates are based largely on geological observations after limited exploratory drilling especially those for Western States. Future exploration is not likely to add much to the solid-fuel reserve, and revisions may be downward as more data are obtained in the various coalfields.

Therefore, to compare fuels reserves the quantities should be expressed in a common energy unit, such as British thermal units, and indicate whether they refer to proved, measured, or indicated material recoverable by current methods. Proved reserves of oil and gas meet the last qualifications. On the other hand, estimates of recoverable coal include considerable quantities of inferred and not proved material, as well as beds from 14 to 28 inches thick or 2,000 to 3,000 feet below the surface and thus not economic to mine at present. The Federal Geological Survey, on the basis of existing data and its reestimation of reserves in 10 States, concluded that one-fourth of the recoverable reserve (see table 6) would fairly represent the proved (measured and indicated) reserve of coal commercially recoverable by current production methods. Estimates of the total inferred recoverable reserves of petroleum and natural gas are compared in table 6 with the minable reserves of coal (including measured, indicated, and inferred) without reference to the cost of mining as a measure of relative reserves of the respective fuels. Column 1 of this table gives the proved (measured and indicated) reserve of coal now commercially minable, proved reserves of petroleum and natural gas, and of oil potentially recoverable from oil shale deposits averaging not less than 30 gallons of oil a ton.

TABLE 6.—*Estimated recoverable mineral-fuel reserves of the United States, as of January 1960*

Kind of fuel	Reserves, quadrillion Btu		Percent of total fuel reserves	
	Proved	Total potential	Proved	Total potential
Coal	5,400	22,000	87.1	77.2
Petroleum, including natural-gas liquids	215	2,355	3.5	8.3
Natural gas	285	1,100	4.6	3.9
Bitumen from bituminous sandstone	10	60	.1	.1
Oil from oil shale	290	3,000	4.7	10.5
Total	6,200	28,515	100.0	100.0

Column 2 gives the recoverable (equivalent to one-half of the grand total), measured, indicated, and inferred coal reserve without any deduction for thin or deep beds, the unproved reserves of oil and gas estimated on the basis of favorable geological formations, and the estimated potentially recoverable reserves of oil from indicated, measured, and inferred oil-shale deposits averaging not less than 25 gallons of oil a ton.

The estimated total coal reserve (including inferred and difficultly accessible coal) is eight times the reserve of coal recoverable under current conditions. The estimated reserve of total oil and oil from oil shale is about 10 times the estimated proved reserve, and the estimated potential gas reserve is about four times the proved reserve. Obviously, coal is the dominant fuel in both estimates. It represents almost 90 percent of the total energy in the proved reserves and almost 80 percent in the potential reserve estimate. If coal had been used to satisfy the demand for liquid and gaseous fuels in 1963, many times as much coal would have been used as the 477 million tons of bituminous coal, anthracite, and lignite produced that year. This example illustrates the tremendous demands that will be made on the resources of coal, oil shale, fissionable minerals, and other sources of energy as gas and petroleum deposits become depleted. The life of these fuel reserves cannot be estimated because of the many variable factors involved. No one can accurately predict demands, new discoveries, and the effect of further technological developments. Estimates have ranged from 75 to 3,000 years supply for fossil-fuel reserves.

Most bituminous coals in the Western States are free burning and noncaking. Some of them are slightly caking but do not become plastic enough to form coke strong enough for blast furnace use.

Relatively small reserves of good coking coal occur in the Trinidad-Raton field of southern Colorado and northern New Mexico. This coal has been used for some years for making metallurgical coke. Bureau of Mines engineers estimate the reserve of coking coal in beds 3 feet and more thick as 850 million tons for the Trinidad field and 600 million tons for the Raton field. These estimates are made on the basis of Federal Geological Survey and other data.

Another coking-coal reserve of probably greater extent but poorer coking properties occurs in the Book Cliffs field of eastern Utah and western Colorado. The Sunnyside beds in Utah are supplying the coke ovens at Provo and Geneva, Utah, and Fontana, Calif. This coal has a high oxygen content and approaches the limit of suitability for making metallurgical coke with adequate physical properties for blast furnace use.

Some strongly coking, low-sulfur coals occur in Pierce and Kittitas Counties, Wash., but, unfortunately, they are high in ash and difficult to mine owing to pitching and faulting of the beds.

SOURCES OF STATISTICAL INFORMATION

The principal sources of statistical information on the bituminous-coal industry are Bureau of Mines publications, most of which are based upon detailed reports of production, mine operation, and distribution furnished by the producers. Additional information is obtained from sales agents, distributors, railroads, retail dealers, traffic associations, equipment manufacturers, consumers, and from other Government agencies such as the U.S. Department of Labor, the U.S. Department of Commerce, the Federal Power Commission, the Interstate Commerce Commission, and State mining departments. All of the economic phases of the coal industry are covered with the possible exception of cost of production. Information on detailed costs of production has been collected only when required by act of Congress for administrative purposes; there has been no requirement in recent years.

PRODUCTION, CONSUMPTION AND TRADE

Production

Through the turn of the century, the bituminous coal industry grew rapidly, almost doubling its production and capacity every 10 years (see table 7). From 1890 to 1910, production increased from 111 million to 417 million tons; it reached a wartime peak of 579 million tons in 1918. The number of mines and employees increased from 2,500 mines and 240,000 employees in 1875 to 9,300 mines and 705,000 employees in 1923. The value of production, at the mines, increased from $116 million in 1895 to over $2 billion in 1920.

From 1920 to the early 1930's, however, the general trend of production was downward—to a low of approximately 310 million tons in 1932. The number of mines and employees dropped to 5,400 and 406,000, respectively, and value at the mines declined to $407 million. The steady, normal growth of the industry came to a halt and gave way to excess capacity, which resulted in a severe depression for coal.

Not until 1940 did the industry as a whole emerge from the depression, following the passage of the Bituminous Coal Act of 1937 and the beginning of heavy war requirements. Production increased to a wartime peak of 620 million tons. To meet the heavy demands for energy during the postwar rehabilitation period, including the highest demands in history for exportation of U.S. coal, production climbed to its alltime peak of more than 630 million tons in 1947. Value f.o.b. mines in 1948 reached almost $3 billion, and the number of mines in 1950 exceeded 9,400. From these pinnacles, however, the drop has been severe, even disastrous for many mining companies and miners. Output in 1961 fell to 403 million tons, second lowest since the prewar depression year of 1939, having dropped previously to 392 million tons in 1954. Since 1961 the bituminous coal mining industry has staged a sizable recovery, reaching outputs of 422 and 458 million tons in 1962 and 1963, respectively. In 1963 the number of mines was 7,940, and value f.o.b. mines amounted to over $2 billion. Employment declined to 141,000.

Although an excess of coal-producing capacity is a bulwark of safety in emergencies, at other times it is a depressing factor in operations of the industry. On the basis of a 280-day work-year, capacity in 1923 was 885 million tons (565 million produced); in 1932, 594 million (310 million); in 1944, 624 million (620 million); and in 1963, 627 million (459 million). In 1944 most of the factors essential for capacity production were present, including a maximum supply of railroad cars and 6 to 7 days of operation per week. Because of the intangibles and complexities involved, attainable production is something less than calculated capacity.

TABLE 7.—*Growth of the bituminous-coal- and lignite-mining industry in the United States*

Year	Production (short tons)	Average value per ton	Number of mines	Men employed	Short tons per man-day	Percentage of underground production mechanically loaded	Percentage of total production	
							Mechanically cleaned	Mined by stripping
1918	579,385,820	$2.58	8,319	615,305	3.78	----------	3.8	1.4
1923	564,564,662	2.68	9,331	704,793	4.47	0.3	3.8	2.1
1928	500,744,970	1.86	6,450	522,150	4.73	4.5	5.7	4.0
1930	467,526,299	1.70	5,891	493,202	5.06	10.5	8.3	4.3
1931	382,089,396	1.54	5,642	450,213	5.30	13.1	9.5	5.0
1932	309,709,872	1.31	5,427	406,380	5.22	12.3	9.8	6.3
1933	333,630,533	1.34	5,555	418,703	4.78	12.0	10.4	5.5
1934	359,368,022	1.75	6,258	458,011	4.40	12.2	11.1	5.8
1935	372,373,122	1.77	6,315	462,403	4.50	13.5	12.2	6.4
1936	439,087,903	1.76	6,875	477,204	4.62	16.3	13.9	6.4
1937	445,531,449	1.94	6,548	491,864	4.69	20.2	14.6	7.1
1938	348,544,764	1.95	5,777	441,333	4.89	26.7	18.2	8.7
1939	394,855,325	1.84	5,820	421,788	5.25	31.0	20.1	9.6
1940	460,771,500	1.91	6,324	439,075	5.19	35.4	22.2	9.2
1941	514,149,245	2.19	6,822	456,981	5.20	40.7	22.9	10.7
1942	582,692,937	2.36	6,972	461,991	5.12	45.2	24.4	11.5
1943	590,177,069	2.69	6,620	416,007	5.38	48.9	24.7	13.5
1944	619,576,240	2.92	6,928	393,347	5.67	52.9	25.6	16.3
1945	577,617,327	3.06	7,033	383,100	5.78	56.1	25.6	19.0
1946	533,922,068	3.44	7,333	396,434	6.30	58.4	26.0	21.1
1947	630,623,722	4.16	8,700	419,182	6.42	60.7	27.7	22.1
1948	599,518,229	4.99	9,079	441,631	6.26	64.3	30.2	23.3
1949	437,868,036	4.88	8,559	433,698	6.43	67.0	35.1	24.2
1950	516,311,053	4.84	9,429	415,582	6.77	69.4	38.5	23.9
1951	533,664,732	4.92	8,009	372,897	7.04	73.1	45.0	22.0
1952	466,840,782	4.90	7,275	335,217	7.47	75.6	48.7	23.3
1953	457,290,449	4.92	6,671	293,106	8.17	79.6	52.9	23.1
1954	391,706,300	4.52	6,130	227,397	9.47	84.0	59.4	25.1
1955	464,633,408	4.50	7,856	225,093	9.84	84.6	58.7	24.3
1956	500,874,077	4.82	8,520	228,163	10.28	84.0	58.4	25.4
1957	492,703,916	5.08	8,539	228,635	10.59	84.8	61.7	25.2
1958	410,445,547	4.86	8,264	197,402	11.33	84.9	63.1	28.3
1959	412,027,502	4.77	7,719	179,636	12.22	86.0	65.5	29.4
1960	415,512,347	4.69	7,865	169,400	12.83	86.3	65.7	29.5
1961	402,976,802	4.58	7,648	150,474	13.87	86.3	65.7	30.3
1962	422,149,325	4.48	7,740	143,822	14.72	85.7	64.3	30.9
1963	458,928,175	4.39	7,940	141,646	15.83	85.8	63.1	31.4

A coal mine is not like a factory, that can be closed and reopened in part or in full to meet fluctuating demands. Because of natural conditions of water and gas accumulations, roof falls, and similar problems, particularly in underground mines, maintenance of idle or only partly used mines is costly. Coal must therefore be sold at almost any price to keep the plants going, to benefit from the advantages of steady output, and to hold out as long as possible for a change to the better. Only when prices are not commensurate with costs and when capital investment has been drained, do many mines close.

Increased efficiency in production and the ability of the industry to absorb some of the increased costs of mining have resulted from greater mechanization. As a further result, new and modernized mines generally are larger than older, nonmechanized mines, and many less efficient mines have ceased operation. In 1924, when less than 1 percent of underground production was loaded mechanically, only 18 percent came from mines having an annual output of 500,000 tons and over. By 1963 the mines in this size category, which represented only 2.8 percent of the total number of mines, produced 53 percent of the total production. In contrast, by 1963, mines producing less than 10,000 tons per year constituted 56 percent of the total number of mines and accounted for only 4 percent of total production. The intermediate mines, representing 37.2 percent of the total number of mines, accounted for 42 percent of total production in 1963.

Because of geographic and other factors, the industry did not lend itself well in the past to combined ownership among comparatively few large concerns, as is common in many other major industries. There are some large coal companies, however, and in recent years there have been some significant consolidations among companies. Nevertheless, there are still over 7,900 mines.

Besides commercial mines which sell their product in the competitive market, the industry includes many so-called captive mines, owned and operated by parent companies primarily to supply their own coal requirements. These mines furnished 14 percent of total U.S. production in 1963. The principal owners of captive mines are steel companies, electric power utilities, railroads, coke plants, and clay-product companies.

The rapid increase in mechanization in a comparatively short period, loss of markets to competing fuels, and increased efficiency in burning coal caused reductions in the number of men employed by the coal industry. Although em-

ployment dropped from a peak of 705,000 employees in 1923 to 142,000 in 1963, productivity increased from 4.47 to 15.83 tons per man per day. The latter figure is an average of 12.78 tons for underground, 38.87 for auger, and 28.69 for strip mining. Correspondingly, mechanical loading of coal underground increased from less than 1 percent in 1923 to 85.8 percent in 1963 and coal stripping from 2 to over 31 percent.

Consumption

Increased availability and consumption of petroleum and natural gas have brought drastic changes in coal utilization. Bituminous-coal and lignite consumption dropped from a peak of 594 million tons in 1943 to 367 million tons in 1958, but since has been on an upward trend (see table 8).

From 1944 to 1963 the coal industry lost 315 million tons of annual consumption in the following markets: 132 million tons formerly used by railroads; 98 million formerly sold by retail dealers; 49 million formerly used for general industrial purposes, excluding electric power utilities; 8 million formerly used by steel and rolling mills; and 28 million tons at coke plants. Over the same period, however, two groups increased their annual consumption of bituminous coal: Electric power utilities used 132 million tons more, and cement mills took 4 million tons more.

Over 40 percent of the total drop resulted from conversion of locomotives to diesel power. Experimentation with a gas turbine using coal as fuel is now in process in an attempt to recover at least some of the lost railroad market.

The decline of coal in the total energy market is indicated further by the fact that as late as 1945 coal (bituminous, lignite, and anthracite combined) contributed over 50 percent of our total energy supply, whereas by 1963 it contributed only 22.3 percent of the annual new supply (see figs. 1 and 2). From 1945 to 1963 petroleum and natural gas increased their contribution from 46 to 74 percent of the total supply. Waterpower remained constant at approximately 4 percent.

TABLE 8.—*Consumption of bituminous coal and lignite, by consumer class, with retail deliveries in the United States*

[Thousand short tons]

Year	Electric power utilities [1]	Bunker, foreign and lake vessel [2]	Railroads (class I) [3]	Manufacturing and mining industries					Retail deliveries to other consumers [6]	Total of classes shown [7]
				Beehive coke plants	Oven coke plants	Steel and rolling mills [4]	Cement mills	Other manufacturing and mining industries [5]		
1933	27,088	2,298	72,548	1,408	38,681	14,129	2,760	81,377	77,396	317,685
1934	29,707	2,423	76,037	1,635	44,343	15,391	3,457	87,314	83,507	343,814
1935	30,936	2,683	77,109	1,469	49,046	16,585	3,456	94,598	80,444	356,326
1936	38,104	3,052	86,391	2,698	63,244	19,019	4,711	111,030	80,044	408,293
1937	41,045	3,433	88,080	4,927	69,575	18,148	5,182	124,056	76,331	430,777
1938	36,440	2,310	73,921	1,360	45,266	11,877	4,413	94,196	66,498	336,281
1939	42,304	2,764	79,072	2,298	61,216	13,843	5,194	100,637	68,770	376,098
1940	49,126	2,989	85,130	4,803	76,583	14,169	5,559	107,864	84,687	430,910
1941	59,888	3,304	97,384	10,529	82,609	15,384	6,735	121,880	94,402	492,115
1942	63,472	3,226	115,410	12,876	87,974	14,722	7,462	132,767	102,141	540,050
1943	74,036	3,042	130,283	12,441	90,019	15,864	5,842	142,149	120,121	593,797
1944	76,656	3,069	132,049	10,858	94,438	15,152	3,767	131,498	122,112	589,599
1945	71,603	3,192	125,120	8,135	87,214	14,241	4,203	126,562	119,297	559,567
1956	68,743	2,632	110,166	7,167	76,121	12,151	6,990	117,732	98,684	500,386
1947	86,009	3,087	109,296	10,475	94,325	14,195	7,919	123,928	96,657	545,891
1948	95,620	2,552	94,838	10,322	96,984	14,193	8,546	110,060	86,794	519,909
1949	80,610	2,056	68,123	5,354	85,882	10,529	7,966	96,629	88,389	445,538
1950	88,262	2,042	60,969	9,088	94,757	10,877	7,923	95,862	84,422	454,202
1951	101,898	2,220	54,005	11,418	102,030	11,260	8,507	103,188	74,378	468,904
1952	103,309	1,839	37,962	6,912	90,702	9,632	7,903	93,637	66,861	418,757
1953	112,283	1,839	27,735	8,226	104,648	8,764	8,167	95,160	59,976	426,798
1954	115,235	1,244	17,370	980	84,411	6,983	7,924	77,115	51,798	363,060
1955	140,550	1,499	15,473	2,869	104,508	7,353	8,529	89,611	53,020	423,412
1956	154,983	1,470	12,308	4,043	101,870	7,189	9,026	93,302	48,667	432,858
1957	157,398	1,364	8,401	3,473	104,547	6,938	8,633	87,202	35,712	413,668
1958	152,928	955	3,725	1,017	75,563	7,268	8,256	81,372	35,619	366,703
1959	165,788	969	2,600	1,827	77,354	6,674	8,510	73,396	29,138	366,256
1960	173,882	945	2,101	1,640	79,375	7,378	8,216	76,487	30,405	380,429
1961	179,629	770	[8]	1,496	72,385	7,495	7,615	77,280	27,735	374,405
1962	190,833	687	[8]	1,339	72,923	7,319	7,719	78,766	28,188	387,774
1963	209,038	670	[8]	1,613	76,020	7,401	8,138	82,797	23,548	409,225

[1] Federal Power Commission.

[2] Bureau of the Census, U.S. Department of Commerce. Ore and Coal Exchange.

[3] Association of American Railroads. Represents consumption of bituminous coal and lignite for all uses, including locomotive, powerhouse, shop, and station fuel.

[4] Estimates based upon reports collected from a selected list of representative steel and rolling mills.

[5] Estimates based upon reports collected from a selected list of representative manufacturing plants.

[6] Estimates based upon reports collected from a selected list of representative retailers. Includes some coal shipped by truck from mine to final destination.

[7] The total of classes shown approximates total consumption. The calculation of consumption from production, imports, exports, and changes in stocks is not as accurate as the "Total of classes shown" because certain significant items of stocks are not included in year-end stocks. These items are: Stocks on Lake and Tidewater docks, stock at other intermediate storage piles between mine and consumer, and coal in transit.

[8] Canvass discontinued.

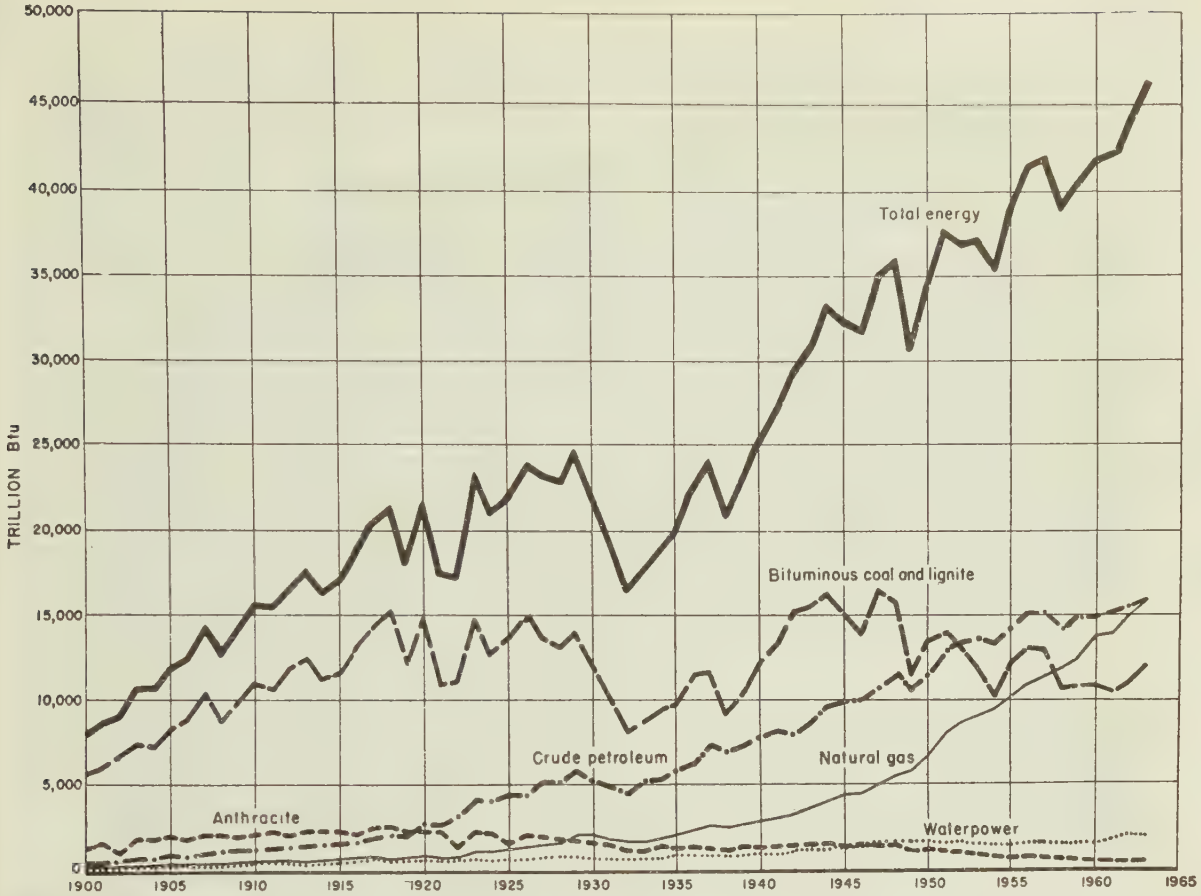

FIGURE 1.—Production of Mineral Energy Fuels and Energy From Waterpower in Continental United States.

Trade

The United States is both an importer and exporter of bituminous coal. Most of the imported coal comes from Canada and goes to a few States—from British Columbia to Washington, Montana, and Idaho, and from Nova Scotia to Maine and New Hampshire. The volume of imported coal is not great, however, compared with exports; it amounted to only 172,000 tons in 1963.

For many years Canada has been the principal customer for U.S. bituminous coal, averaging around 12 million tons a year during the past 5 years. Overseas exports, chiefly to Europe and Japan, have fluctuated widely, influenced primarily by changing rates of economic growth following postwar rehabilitation, high costs of indigenous production abroad, lack of adequate coking coals for the steel industry, vessel rates, and emergencies such as the Suez Canal crisis and severe winters. The availability of high-quality U.S. coal for export at economical prices is a result of the high productivity and efficiency of U.S. coal mining.

Total bituminous exports fluctuated between a peak of 76 million tons in 1957 and 35 million tons in 1961 during the past 7 years. They approximated 48 million tons in 1964.

In 1963 the six member countries of the European Coal and Steel Community (Belgium, France, Italy, Luxembourg, Netherlands, and West Germany) imported 21.4 million tons of coal from the United States (41.7 million tons in 1957), representing 85 percent of the total U.S. exports to Europe and 45 percent of world shipments. West Germany and Italy received 5.5 and 7.6 million tons, respectively, as compared to 15.5 and 8.8 million tons in 1957.

U.S. coal exports to Japan in 1963 (6 million tons), principally for the production of coke for blast furnaces, were double those of 1954 (3 million tons).

Notwithstanding increasing energy demands, coal production in most western European countries has been declining in recent years. This is due largely to the increased use of oil for industrial purposes, and to the discovery of natural gas in northeastern Europe. Nevertheless, because of the increasing energy demands and requirements for good quality coking coals in Japan, there are appreciable potentials for the increased exportation of U.S. coal.

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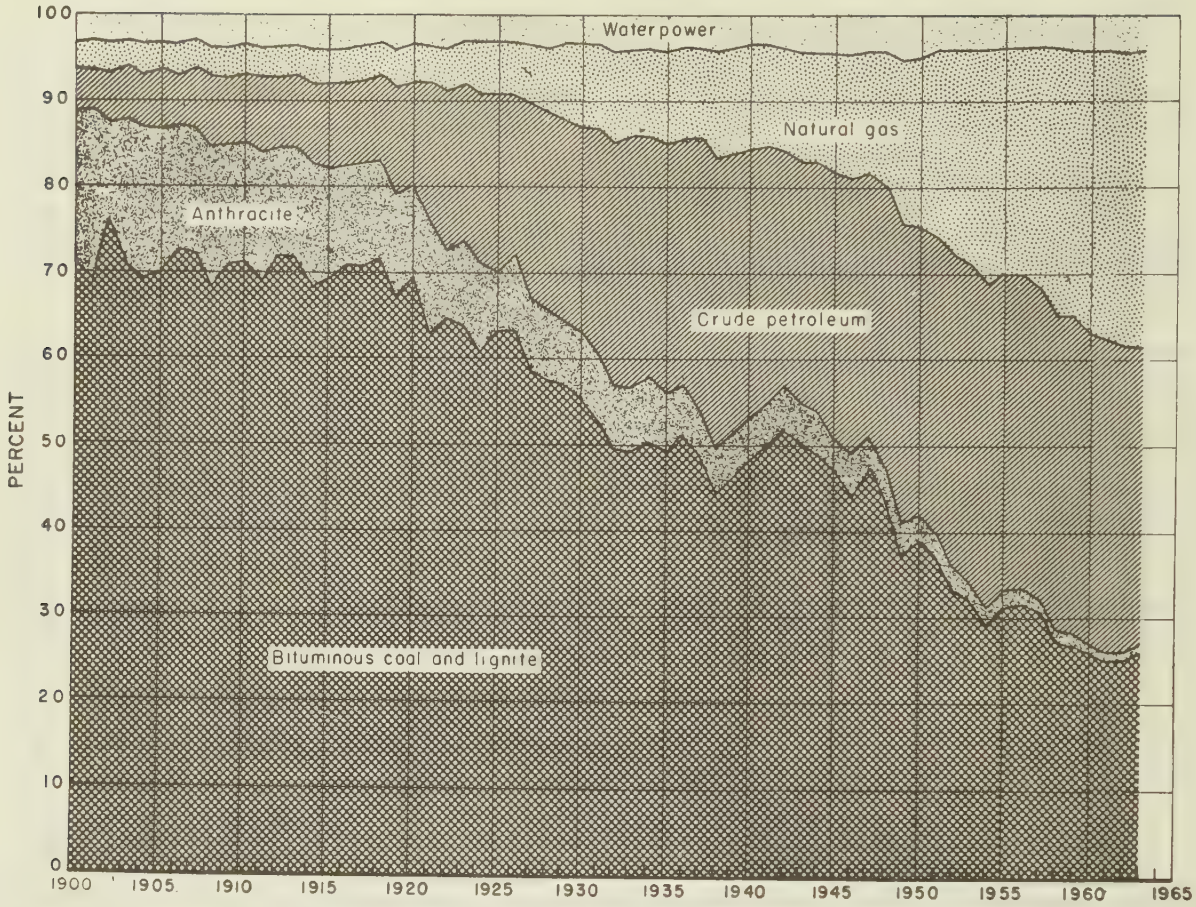

FIGURE 2.—Percent of Total Production of British Thermal Units Equivalent of Mineral Fuels and Energy From Waterpower in Continental United States

STRATEGIC CONSIDERATIONS

Coal is of vital importance in national emergencies, both as a source of energy and as a raw material for military and civilian requirements. The availability of adequate quantities of proper sizes and kinds of coal and their correct distribution aid in the timing and success of military programs. For the production of iron, steel, and electric power in the huge quantities required for national defense, coal is indispensable. Similarly, it is essential for manufacturing expansion generally, for space heating, and for the production of chemical raw materials such as toluene (a prime ingredient of explosives), benzene (vital in the manufacture of aviation gasoline and synthetic rubber), tar derivatives (used in the manufacture of a variety of important chemical products such as dyes, drugs, creosote oil), and fertilizers.

In manufacturing, 6 pounds of coal are used to make 1 pound of smokeless powder, 2 tons for a 1-ton bomb, and 220 tons for a modern tank. In addition to expanded requirements for coal for the kinds of uses to which it is normally put, coal must replace fuel oil when petroleum is diverted to more strategic uses and when oil supplies are limited because of transportation difficulties, including curtailment of offshore shipments because of submarines.

Coal is a bulk commodity consumed by the hundreds of millions of tons; in turn, it requires other materials and services that are scarce in national emergencies. Thus, the best preparation for defense (with regard to any basic commodity) is reasonably healthy operation during peacetime. To produce and distribute coal in wartime, adequate manpower must be available at mines, as well as transportation facilities, particularly open-top railroad cars. Stockpiling and distribution must be modified to allow for diversions to war industries, defense-production centers, and military bases. These other problems require planning and coordination of industry and Government, including the forecasting of requirements for coal, productive capacity, manpower equipment, supplies, and services so that the huge quantities required for

defense will be available when and where needed.

COST AND PRICE OF COAL

Two controlling forces operate to keep coal prices at levels that are not always commensurate with costs of production or with the attainment of reasonable profits—intraindustry competition and competition with oil, natural gas, and nuclear energy. Whereas even though under pressure of competition from only one of these two forces, coal prices might rise somewhat in keeping with increases in costs or with required profit margins, pressure from both makes price rises difficult under all but exceptional market conditions.

Current quotations on soft-coal prices at the consumer level are approximate but do throw some light on the market situation. Except for the annual average cost of bituminous coal at merchant coke ovens, the Bureau of Mines does not collect data on market prices of coal. The principal Government activities in this respect are (1) average wholesale and retail prices of soft coal, based on sampled coverage, as published by the Bureau of Labor Statistics; (2) monthly publication by the Interstate Commerce Commission of the average cost of railroad fuel purchased, at the mines; and (3) Federal Power Commission information pertaining to the cost of coal at electric power utilities. The coal-trade journals published some posted current wholesale prices, f.o.b. mine, usually in terms of high and low quotations.

The most valuable index of the trend of prices at the mines is the annual figures of average value per ton published by the Bureau of Mines. These data are on a national, State and county basis and are classified according to the method of mining. The national average value f.o.b. mines has fluctuated widely from year to year, although it remained remarkably constant from 1948 through 1958, ranging from $4.99 per ton in 1948 through $4.50 in 1955 and $5.08 in 1957 to $4.86 in 1958. Since 1958 the average value has declined each year, having reached $4.39 per ton in 1963, the lowest level since 1947. For the 6 years ending 1963, the average value dropped 11½ cents per year. The main reason for these declines, even though labor and other costs have increased during the last period, is increased productivity and competition with other fuels.

There are wide variations in the average value f.o.b. mines among States and counties. Mining conditions, the quality of coal, the distance to markets, the method of transportation, and the competitive situation in the energy market largely explain these variations. The same factors also cause wide differences in costs and prices among producing companies. For example, the principal price factor above f.o.b. mine values is cost of transportation. For rail shipments it amounts to some 74 percent of the f.o.b. mine price. Those producers who are favored by circumstances often have a stabilizing influence on the market.

Such factors as excess capacity and production strongly influence market prices. Both encourage strong intraindustry competition, certain price instability, and lower profits than otherwise might be available. As little coal is stored at producers' facilities, particularly at rail-shipping mines, and as producers generally must dispose of all their sizes, both prepared and resultant, if they are to stay in operation, coal must move into the market within a reasonable time after production. Mines sometimes produce too much of the resultant sizes and dispose of them at prices that disregard production costs. These surpluses can have a depressing effect on prices quite out of proportion to the amount of such coal available.

The shift in emphasis from domestic to industrial uses for coal has brought about some fundamental changes in coal sizes which, in turn, have affected the economics of the industry. Whereas in past years the large market for domestic sizes of coal carried premium prices, and therefore the major share of financial return to the industry, the present and future market will be preponderantly for industrial sizes. Because of competitive pressures, the coal industry has not been able fully to recast its pricing system to match the heavy shift to industrial sizes and thus to bolster its tenuous margin of profitability, nor does it have the flexibility of competitive fuels industries of spreading its pricing pattern over a multiplicity of products.

TAXES

Federal taxes paid by the bituminous coal industry vary with the profitableness of the industry. For more than a decade prior to 1940 the industry operated at a deficit. In 1961, the latest year for which figures are published, and in which 403 million tons were produced, the bituminous coal industry paid $26 million in taxes, and profit after Federal taxes amounted to $31 million. Bituminous coal producers, when computing Federal income tax, are allowed a percentage depletion deduction calculated at 10 percent of gross income from the producing property, but not more than 50 percent of the net income from such property.

TRANSPORTATION

Almost three-fourths of all coal leaves bituminous mines via railroads at rates that add

nearly 74 percent to the cost of the coal at the mines.

Railroads have been the principal means for shipping bituminous coal since their development. In recent years this method of transporting coal has declined appreciably owing largely to increased movement by water and truck from the mines to final destinations. Approximately 40 to 87 million tons of coal is dumped annually at Atlantic coast tidewater piers and transported by water to ports in the United States or exported overseas. In the past decade a range of from 44 to 58 million tons annually has been dumped at lower Lakes Erie, Ontario, and Michigan ports and transported by water to the West North Central States, New York, and Canada. Some of this coal is transshipped by rail or truck to final destination.

Motor trucks for transporting coal appeared immediately after World War I but were not an outstanding factor until the late 1920's. By the middle 1930's trucks had become an important means of transporting coal from mines not only to final destination but also to tipples, railroad sidings, or waterways for further shipment. The development of bigger and better trucks and improved highways has stimulated the growth of truck shipments to final destinations. As railroad freight rates for coal are not strictly proportional to distance and as freight rates for short hauls are higher than for long ones, trucks are used increasingly for short-haul traffic.

Although some of the earliest shipments of bituminous coal were made by river, the major movement by river awaited the growth of large consumers on water, particularly the steel industry on the Monongahela River near Pittsburgh, and in more recent years the aluminum industry in the Ohio River Valley and the Tennessee Valley Authority installations in the Tennessee River Valley. Although in 1963, bituminous coal was shipped from mines by way of 10 rivers and the Inland Waterway, the largest movement was on the Monongahela River. The proportion shipped from mines by water, including the tonnage trucked to water, has grown from 4 percent of total production in 1933 to 11 percent in 1963. Part of this growth represents increased shipments on rivers other than the Monongahela. Like rail shipments, river shipment is not necessarily to a final destination. A considerable tonnage, particularly in the Cincinnati area, is transshipped from the Ohio River to final destination by railroad or truck.

An important development in shipping bituminous coal has been the trucking of coal from mines to railroad sidings or to waterways for further shipment. This relatively new use of trucks made possible the opening of many small mines and even of larger strip mines.

Some railroad companies have established, while others are planning, significant changes in methods of transporting coal to large consumers. These changes include the unit train and modifications of the unit train concept, in which trains consisting entirely of coal cars move quickly from the mining areas to the consumers' plants, with greatly increased efficiency in the utilization of railroad equipment and sizable reductions in cost. There have been some notable railroad freight rate reductions as a result of these new methods, amounting to as much as $1.50 per ton in some cases. The expansion of these concepts will enhance coal's competitive position in important energy marketing areas.

Because of the importance of the cost of transportation, pipeline transmission of coal in water has been developed. The Consolidation Coal Co. constructed a 108-mile coal pipeline from a mine in eastern Ohio to the East Lake powerplant of the Cleveland Electric Illuminating Co. near Cleveland. The $13 million pipeline carried 7 million tons of coal slurry before it ceased operation on a standby basis in May 1963 after railroads made sharp cuts in coal freight rates.

Technological advancement in the long-distance transmission of electric energy continues to result in more large-scale electric generating capacity near or at mine sites.

RESEARCH

Every country in which extensive deposits of coal occur is interested in the effective utilization of these valuable natural resources and is, therefore, conducting a variety of programs geared toward the realization of this objective. In each of these countries there are a variety of government, industrial, university, and/or private organizations conducting research programs on the properties of coal, its production and preparation, utilization as a fuel, and conversion to other forms. The interest, scope, and emphasis on particular investigations are primarily influenced by national conditions, current markets and anticipated needs, as well as the facilities of each research organization.

In the United States there are a variety of laboratories engaged in coal research programs. The Department of the Interior is responsible for more than one-half of the effort in this area, about equally divided between the Bureau of Mines and the Office of Coal Research.

One of the primary functions of the Bureau of Mines is to improve the Nation's ability to meet the energy needs of an expanding economy and

to insure the Nation's security. Within the framework of this objective, the Bureau's projects in coal research and development serve to: (1) increase efficiency and economic development of the industry, including new uses, (2) conserve resources through prevention of waste, (3) investigate mineral fuels belonging to or for the use of the United States, and (4) improve health and safety conditions in the mineral industries. Efforts to realize these objectives involve a variety of coal studies, ranging from fundamental research through development of processes and products. The diversity of problems under investigation by the Bureau can be illustrated by the programs now underway in the Bureau's laboratories, located in important coal-producing centers. For example, the Bureau of Mines laboratories in Pittsburgh and Bruceton, Pa., are conducting programs such as those on coal mining, health and safety, analysis, preparation, combustion, carbonization, conversion to liquid and gaseous fuels, stream pollution, and fundamental studies; in Morgantown, W. Va., on the coal-fired gas turbine and low-temperature tar; at Denver, Colo., western coals investigations including carbonization; at Grand Forks, N. Dak., lignite investigations; at Seattle, Wash., preparation; at College Park, Md., sampling, boiler-water research, and fuel economy service; at Juneau, Alaska, resources studies; and sampling and analysis at Anchorage, Alaska.

The Office of Coal Research undertakes research which holds the greatest potential promise for achieving benefits to the coal industry in new production and markets. Its research, all of which it contracts with outside organizations, covers many disciplines including mining, combustion, conversion processes, and economic and marketing research.

Apart from the Department of the Interior activities in coal research, there are a large number of organizations conducting programs directly related to and supplementing the Bureau's activities in each of the broad areas previously mentioned. Research on coal properties, and studies designed to extend the information available on U.S. coal reserves are being conducted by university and State geological laboratories, such as Illinois State Geological Survey, Ohio Geological Survey, Ohio State University, Pennsylvania State University, and West Virginia University. The production, preparation, and utilization of coal as a fuel are of primary importance to industry and are the objects of study by private and industrial organizations, as well as by university and State laboratories, with many of the latter programs sponsored or supported by industrial groups. In addition to the organizations cited above, interesting and important programs are being conducted by Bituminous Coal Research, Inc., and universities and private concerns in various parts of the country. The variety and scopes of such investigations, and the names of the particular organizations conducting such programs are described each year in a review published in the coal press.

In European countries, coal research programs are administered primarily by government research organizations. The activities of these organizations reflect in scope those of the Federal Bureau of Mines but are directed primarily towards the application of new tools or techniques to local reserves and economic conditions. Thus, the variations in coal quality and availability from country to country as well as the industrial economy of each country are reflected in the emphasis on and type of programs conducted by the counterpart organizations abroad.

In Western Europe, the United Kingdom conducts the largest and most diversified program of coal research. In Great Britain and the Commonwealth Territories, considerable attention has been directed to the exploitation of thinner seams than are mined in the United States and the utilization of fine and low-rank coals, such as lignite. In addition to and related to these investigations, a variety of programs concerned with the advancement of knowledge on the fundamental properties and structure of coal, coal mining (including health and safety), sampling and analysis, preparation, combustion, gasification, and hydrogenation are in progress. As in the United States, attention has also been directed to the possibility of converting coal to liquid and gaseous fuels and plants designed to evaluate the potential application of the Fischer-Tropsch and other processes have been constructed and operated.

In France, the Netherlands, and West Germany, research programs on coal also closely parallel in scope the programs and interest of the Bureau of Mines and other U.S. research organizations.

Cerchar (Centre d'Etudes et Recherches des Charbonnages de France), in France, and Inichar (Institut National de l'Industrie Charbonniere), in Belgium, are the organizations responsible for the greatest effort in coal research in each of these countries, and could also be likened, in scope and interest, to the Bureau of Mines. As in the United States, a number of universities in each of these countries are also conducting specialized research programs on coal. In West Germany, the Steinkohlenbergbauverein conducts the largest number of programs, which is supplemented by the activities of other research organizations and university laboratories.

In the U.S.S.R. and satellite countries, in

India, mainland China, and Japan, research programs administered by government organizations are broad in scope and cover each area described earlier. Of these countries, the U.S.S.R. is probably the most active and has the largest integrated program related to the development of its coal industry. Much emphasis has been placed on the development of new mining equipment and methods and new applications for coal. A concerted effort has been made in the U.S.S.R. to increase productivity, to insure maximum exploitation, and to utilize reserves which, in this country, would be considered uneconomical. Thus a large-scale program for the underground gasification of coal, abandoned on the basis of economics by research organizations in other countries, is still being pursued in the Soviet Union. Other programs in the U.S.S.R., and each of the other countries mentioned, parallel those of the United States.

OUTLOOK

Although the production of bituminous coal and lignite dropped seriously after the post-World War II period of economic rehabilitation and coal's share of the total energy market declined markedly, it reached a turning point in 1961, after which output started an upward trend.

Coal remains as the major supplier of industrial energy, principally because of the increased consumption of coal for steam generation at electric power generating plants. It is indispensable to industrial expansion in national emergencies.

Although future coal production will depend in great part on the degree of availability and consumption of oil, natural gas, and nuclear energy, it is believed that coal has reached, and passed, its lowest point, and that the national economy is undergoing a transitional period in which the demand for all kinds of energy will increase greatly. Our population continues to grow rapidly, and per capita energy requirements are advancing. Business and industry should expand accordingly. The gross national product (the total national output of goods and services) is increasing at about 4 percent per year, and the tremendously accelerating growth of electric power continues unabated. All of these factors point to a considerable expansion in the steel industry, which may be reflected in an increased demand for coke. Continuing improvements in coal technology should result in further reductions in costs of production and increased efficiencies of utilization. There are certain limitations in the sources of competing fossil fuels to supply the expanding energy demand. It is expected that new uses for coal will be found in the hydrogenation, gasification, gas synthesis, and carbonization processes, and in the production of nuclear fuels. In view of these and other factors, it has been forecast that the demand for energy will be so greatly expanded that yearly coal production may reach 775 to 800 million tons within the next 15 years.

PROBLEMS

During times of intense downward pressures on prices, high maintenance costs of idle facilities, and efforts to avoid loss of investments force coal mining companies to continue operating while anticipating a change to better conditions, even though income from sales may be below costs of production; under these conditions operations are maintained only by using up capital.

The pricing of coal is restricted by costs of production and competition with other fuels. Coal does not enjoy the flexibility of some competing fuels for spreading its prices over a multiplicity of products for the reason that coal is a singular product. The importation of other fuels poses some special competitive problems for coal.

The principal problem in relation to coal output and consumption currently and for the future is the development of means to enable coal to compete more favorably with oil, natural gas, and nuclear energy. The basic challenge is to develop advanced technology for further reducing costs of coal production and transportation and to develop methods of handling and burning coal that will provide increasing efficiencies and greater convenience in the use of coal and in the disposal and utilization of its waste products.

Improvements in and new methods of mining are needed to permit extraction of coal at lower cost, with increased safety to the workers, and with consideration of conservation principles and objectives. Effective degasification of gassy mines ahead of mining will relieve a hazard to the mining crews and a major retardant to the continuity of mining operations. Nothwithstanding improved safety practices and requirements, roof falls, the formation and ignition of coal dust, and other hazardous conditions associated with underground mining result in serious accidents, deaths, and losses each

year. Acid mine water drainage from worked-out mines, or sections of mines above the drainage level, is a serious water-pollution problem.

Increased mechanization in the extractive and preparation processes has resulted in the output of finer-sized materials with greater quantities of associated impurities. The mining and supplying of coals that are acceptable for power plant, metallurgical, or other uses imposes a variety of problems. In many cases, more intensive preparation and careful blending of coal are required to produce coals of comparable quality to that used in the past. Current methods of dewatering and thermal drying are relatively expensive. Large quantities of potentially valuable products are lost with the washery refuse and effluents from preparation plants, especially fine coals that cannot be salvaged economically from the waste water. These losses may increase with the expansion of production and will require the development of effective disposal and utilization methods as lack of adequate disposal areas and enforcement of air and steam pollution ordinances curtail current discharging practices.

Because of the increased availability and utilization of petroleum and natural gas, bituminous coal and lignite consumption in the United States has declined from the war-period peak, and there have been some significant shifts in the pattern of utilization. There have been continuing losses in bituminous coal shipments to railroads, retail dealers, bunkers (foreign and lake vessels), and steel and rolling mills (excluding coking coal). However, on the plus side coal consumption by electric power utilities has increased steadily and significantly, and as demands for electric energy continues to grow the increased use of coal by public utilities seems assured. Coal consumption at general industrial plants has been on the increase during the last few years. One of the newer threats to coal is the use of nuclear energy for the generation of electric power. To maintain optimum efficiency of boiler equipment, problems relating to stack-emission and mineral deposits on the convection surfaces of utility steam boilers, which reduce efficiency and limit capacity, remain to be adequately solved.

The emission of air pollutants from coal combustion equipment is a problem of increasingly greater importance. The emission of SO_2, formed when sulfur containing fossil fuels are burned, is of special concern to large cities. One such city has limited the permissible sulfur content of fossil fuels burned within its jurisdiction. There are indications that other State and local governments will enact laws or ordinances designed to minimize air pollution. The Federal Government, under the auspices of Public Health Service is charged with administering the "Clean Air Act of 1964." It is widely recognized that laws by themselves are not sufficient to solve the air pollution dilemma. Industry, as well as the Federal and several State Governments, are conducting research projects to find economical means of solving the problem of increased air pollution which is a result of our increased energy needs.

Transportation costs constitute a significant portion of the price of coal to consumers. To reduce freight costs, there have been sizable shifts to river and truck transportation. The use of unit-trains, which is a relatively new concept in rail transportation, holds great promise in reducing coal freight costs for purchasers or to points using large quantities of coal. In addition, the railroad industry is conducting research on other innovations in coal transportation, including the integral train. These will be very long, special trains of new, larger type cars, for which special types of loading and unloading facilities will be used. Through the substantially increased efficiencies expected, further reductions in coal transportation costs are anticipated.

Extensive application of pipeline transmission of coal would be a significant development. Justification of the costs involved are limited, however, by the need for large-volume coal production and use. Another means of alleviating the problem of coal transportation costs is the long-distance transmission of electricity from generating plants at or near mines, often referred to as coal-by-wire.

New large-scale uses of coal need to be developed. The markets for chemicals, and for gaseous and liquid fuels could provide outlets for substantial quantities of coal. The processing of coal for the independent production of such chemicals and fluid fuels is now uneconomic, however, so that it cannot yet compete on a cost basis with conventional supplies of these products. The development of new, large-scale markets for coal could be realized if the economics of the following processes, all requiring additional research, were modified by adequate new technological developments: (1) production of liquid fuels and chemicals by rigorous hydrogenation of coal; (2) production of organic chemicals by mild hydrogenation of coal; (3) production of liquid fuels and chemicals from water gas; (4) complete gasification of coal by nuclear energy, or alternatively, by conventional reaction with oxygen and steam for making high Btu gas, liquid fuels, and chemicals; (5) improvements in space-heating technology to expand the use of the coal for this purpose.

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BORON

By William C. Miller [1]

IN THE 13th century borax was imported into Europe from Asia for use as a precious-metal flux. Later Italy and South America became the leading producers of borax, which was used chiefly for medicinal purposes. The output of boron minerals in the United States started in 1864. Early production was characterized by the recovery of small quantities of borax from the beds of dry saline lakes. Later the mining of colemanite deposits became important. Today the United States furnishes the bulk of world production from deposits of sodium boron minerals. Sedimentary deposits of borax (tincal) and kernite (rasorite) occur in the Kramer district near Boron, Calif. Borax also occurs in a dry lake deposit at Searles Lake, Calif. Minor quantities of calcium borate minerals, colemanite, and ulexite are produced from bed-type deposits.

Boron minerals are mined by open-pit methods at Boron, Calif., and refined by crystallizing from a hot water solution. At Searles Lake borax is recovered from brines by evaporation and crystallization methods.

Reserves of boron minerals at Boron and Searles Lake, Calif., have been estimated to be sufficient for many years at present rates of depletion.

Boron and boron compounds have numerous uses, including applications in glass, ceramics, welding compounds, soaps and detergents, plasters and paints, starches, fertilizers, steel, nonferrous metals, atomic reactors, radio tubes, solar batteries, abrasives, refractories, chemicals, plastics, motor fuel, antifreeze, insulation materials, adhesives, drugs, and cosmetics.

Boron minerals are relatively inexpensive; however, transportation is a large item of the cost. In 1963 the cost of granular borax at the works was $50 per short ton, whereas the price at the warehouse in New York City was $95 per short ton. Elemental boron, which is costly to produce, is finding a larger market.

Boron minerals and compounds are exported from the United States to many countries. Very small quantities of special boron compounds are imported into the United States.

Much research on boron and boron compounds has been conducted by industry and the Government. The Bureau of Mines is conducting programs on the production and properties of high-purity elemental boron and has studied boron mining problems. Industry is concentrating research on boron polymers, epoxy-boron fibers, and glass-fiber textiles.

The outlook for the continuing growth of boron markets is good. Increased production facilities have been undertaken by the principal producers, and increased consumption of boron products can be anticipated. New products will be made commercially available as a result of achievements in research.

Most of the problems involving boron will stem from marketing rather than from production. The use of boron minerals is inhibited somewhat by transportation costs and the remoteness of production areas from markets.

BACKGROUND

Boron compounds were known and used for many centuries before the element boron was discovered. Three chemists, Joseph Louis Gay-Lussac and Louis Jacques Thenard of France and Sir Humphrey Davy of England discovered the element almost concurrently in June 1808 (*7*, *15*).[2]

The earliest recorded use of borax, the most important compound of boron, was by Asian artisans in the welding and brazing of precious metals and the glazing of pottery. The importation of borax into Europe from Tibet in the 13th century was the start of the modern boron industry. In the middle of the 18th century sassolite was discovered in the hot springs of Tuscany, Italy. Starting about 1828, recovery of boric acid from these hot springs supplied

[1] Commodity specialist.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

much of the world's requirements. Borax mining began in Chile in 1852, and that country became the principal producer. The chief use for borax during this period was for pharmaceutical purposes.

In 1856 borax crystals were discovered in the mud of a small saline lake in Lake County, Calif. Production of borax from saline lakes in northern California started in 1864 and continued for 10 years. Ulexite was found in quantity on the arid lake beds of Nevada in 1870. During the 1870's and 1880's ulexite and borax were recovered from Columbus Marsh and Teel's Marsh in Nevada and from Searles Lake in California, which caused the northern California operations to be discontinued. From 1883 to 1889 borax was obtained from Death Valley (*20*, *21*).

The greater part of the world's supply of borax came from the colemanite deposits in the Calico Mountain district, Calif., between 1887 and 1907. When these deposits were worked out, production was shifted to the Furnace Creek district, adjacent to Death Valley. The colemanite and lake deposits of this district were the principal source of borax from 1915 to 1926.

Since 1927 the rich deposit of borax and kernite ore in the Kramer district of Kern County, Calif., has been the world's principal source of boron (*16*).

Production of borax from Searles Lake, Calif., started in 1874 and continued until about 1893, when playa operations were supplanted by colemanite mining. In 1908 operations at Searles Lake were started again, but output was sporadic. Since 1916 production of borax and various coproducts from Searles Lake brine has been continuous.

When originally imported into the United States from England, borax was a high-priced commodity, used chiefly for pharmaceutical purposes. By 1892 the price was lowered substantially so that borax was used for many other purposes. The most important of the 50 uses listed at that time were as an antiseptic, a meat preservative, soap and cleansers, and an ingredient in tooth and face powder, process used in printing calico dresses, varnish, plaster paint, fireproofing material, and insecticides.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Four domestic firms produced boron minerals in 1963 from bedded and vein deposits and from natural brines. The entire output came from southern California. Total production was 700,183 short tons valued at $54 million. The principal producer, Pacific Coast Borax Division of United States Borax & Chemical Corp., produced kernite (rasorite) and borax (tincal) from a bedded deposit in the Kramer district near Boron, Calif., and colemanite in Inyo County, Calif. The second largest producer, American Potash & Chemical Corp., recovered a substantial quantity of borax from the brine of Searles Lake at Trona, Calif. The West End Chemical Division of Stauffer Chemical Co. recovered borax from the brine of Searles Lake. Kern County Land Co. mined colemanite in Inyo County, Calif.

Other deposits of boron minerals occur in Nevada, Oregon, and California but are not mined at present.

In addition to the producers of boron minerals, there are approximately 50 companies that produce a wide variety of boron products and about 20 companies that produce boric acid.

Outside the United States, Turkey is the leading non-Communist boron mineral producing country (*12*, *13*). Three operating companies produced colemanite from deposits in western Turkey. Etibank, a state mining enterprise, is the principal producer. In 1963, Etibank produced about three-fourths of the total output.

Boric acid is produced from steam vents at Tuscany, Italy, by a state-controlled firm.

In South America the boron production comes from ulexite deposits in Argentina and Chile. Cía Productora de Boratos and Boroquímica Ltda., are the leading producers in Argentina. Borax Consolidated, Ltd., is the only producer in Chile.

DEFINITION OF TERMS, GRADES, SPECIFICATIONS, AND PROPERTIES

Elemental boron has an atomic weight of 10.82, melting point of about 2,300° C and boiling point of 2,550° C. Boron is produced in two forms, amorphous and crystalline. The amorphous variety is a black-to-greenish-yellow powder, whereas the crystalline form is a brittle, shiny, hard solid. Boron is marketed in grades of 90 to 92, 95 to 97, and 99-plus percent purity.

Borax ($Na_2B_4O_7 \cdot 10H_2O$) is purified to grades of 99.5 percent and marketed as decahydrate and pentahydrate. An anhydrous form of borax is also marketed. Borax is available in commercial or technical, U.S.P., and special-quality grades. It is sold in crystalline, granular, or powder form.

Boric acid (H_3BO_3) is manufactured as colorless, odorless crystals. It is sold as commercial or technical, U.S.P., and special-quality

grades. It is available in crystalline, granular, or powder forms.

Boric oxide is a hard, brittle, colorless, transparent glass. It is marketed in powder or granular forms.

Ferroboron is a boron iron alloy containing 0.20 to 24 percent boron. Boron alloys are marketed in a number of grain sizes.

Diborane (B_2H_6) is a gas with a heating value of 31,200 to 33,300 Btu per pound. Pentaborane (B_5H_9) is a liquid with a heating value of 29,000 to 30,400 Btu per pound. Decaborane is a solid with a heating value of 28,200 to 29,300 Btu per pound.

Boron nitride is manufactured as a white, greasy, amorphous-to-flaky solid. It crystallizes in thin hexagonal plates, similar to graphite. Boron nitride has an electrical resistivity of 1,900 ohms per centimeter at 2,000° C and a very low thermal conductivity. It can be obtained in grades of less than and greater than 98 percent purity.

TECHNOLOGY

Many known minerals contain boron, but only a few are commercially valuable as a source of boron. The principal boron minerals are borax (tincal), $Na_2B_4O_7 \cdot 10H_2O$; kernite (rasorite), $Na_2B_4O_7 \cdot 4H_2O$; colemanite (borocalcite), $Ca_2B_6O_{11} \cdot 5H_2O$; ulexite (boronatrocalcite), $CaNaB_5O_9 \cdot 8H_2O$; priceite (pandermite), $5CaO \cdot 6B_2O_3 \cdot 9H_2O$; boracite (stassfurtite), $Mg_7Cl_2B_{16}O_{30}$; and sassolite (natural boric acid), H_3BO_3.

The sodium borate minerals borax (tincal) and kernite (rasorite) constitute the bulk of production in the United States. A small quantity of colemanite and ulexite is also mined. Sodium borate mineral deposits on the public domain can be acquired under the mineral Leasing Act of February 25, 1920. Other minerals, such as colemanite, are open to exploration and purchase under the mining laws of May 10, 1872.

The borate deposit in the Kramer district of California is a large, tabular, irregular mass of bedded crystalline sodium borates ranging from 80 to over 250 feet in thickness. Borax, locally called tincal, and kernite are the principal minerals. Shale beds containing colemanite and ulexite lie directly over and under the sodium borate body (*16*, *20*).

The ore, mined by open pit methods, is blended and crushed to produce a minus ¾-inch refinery feed of nearly constant boric oxide (B_2O_3) content. Weak borax liquor from the refinery is mixed with the crushed ore and heated nearly to boiling point in steam-jacketed tanks to dissolve the borax. Before the concentrated borax liquor goes to a series of thickeners, the solution passes over a vibrating screen to separate the insoluble rock and clay particles. Concentrated solution from the thickeners is filtered and pumped to vacuum crystallizers. One of the crystallizers produces borax pentahydrate, and the other produces borax decahydrate. Crystals are separated from the slurry of borax pentahydrate or decahydrate by automatic centrifuges. From the centrifuges, the crystals are fed to dryers to remove surface moisture. The borax crystals are stored prior to sale or shipment to other divisions for production of anhydrous borax, boric acid, boric oxide, and specialty products.

The Searles Lake Deposit, in the northwest corner of San Bernardino County, Calif., covers about 34 square miles and contains two crystalline salt beds separated by an impervious mud seam 10 to 14 feet thick. The upper crystalline bed ranges from 25 to 40 feet in thickness and the lower bed from 70 to 90 feet. Saturated brine, containing about 35 percent dissolved solids, fills about 45 percent of the volume of each salt bed. The lower salt bed brines contain the higher concentration of borates (*8*, *19–21*).

Two processes are used to recover borax from the brines of Searles Lake. American Potash & Chemical Corp. uses an evaporation process to treat the upper bed brines and a carbonation process to treat the lower bed brines. West End Chemical Division of Stauffer Chemical Co. uses a carbonation process. The operations of the carbonation processes used by the companies are similar.

Most of the borax produced from the Searles Lake brines is by the evaporation process. In this process, the brine goes to the potash plant where sodium chloride (NACl) and burkeite ($2Na_2CO_3 \cdot 3NaSO_4$) are crystallized and separated from the liquor containing potash (KCl) and borax ($Na_2B_4O_7 \cdot 10H_2O$). By cooling the liquor rapidly in special crystallizers, the potash is crystallized and filtered from the solution. The chemistry of the process is complex and care must be exercised to prevent the boron from being crystallized with the potash. Mother liquor from the potash plant and borax (decahydrate) from the carbonation plant is sent to the borax plant. The liquors are fed into large crystallizers containing a thick bed of seed crystals to crystallize the pentahydrate of borax. From the crystallizers the sludge stream is sent to a liquid cyclone and to crude borax filters. The solids from the filters are washed, repulped, and redissolved before being sent to vacuum crystallizers where high-purity borax (decahydrate) or pentahydrate is formed. After the products are dewatered and dried, they are screened to the desired fractions.

In the carbonation process, brine from the lower salt bed is fed into the top of primary carbonation towers where the brine is contacted by carbon dioxide gas which enters the bottom of the towers. Boiler flue gas is used by American Potash and gas from a limekiln is used by West End Chemical. From the primary towers the slurry is sent to secondary carbonation towers to complete the carbonation. Sodium bicarbonate filters remove the soda ash, and the filtrate is blended with additional raw brine before the solution enters vacuum crystallizers where decahydrate borax is crystallized. The slurry containing borax and some sodium bicarbonate is sent to the evaporation plant in the American Potash process. In the West End Chemical process, the slurry is further refrigerated to crystallize the sodium sulfate.

Boron carbide (B_4C) is produced by reacting boric oxide (B_2O_3) with coke in a carbon resistance furnace at 2,600° C. The product is about 99 percent B_4C.

Elemental boron has been produced by fused-salt electrolysis, hydrogen reduction and decomposition of boron compounds, reduction of boron halides with active metals, and reduction of other boron compounds with active metals (*4*, *10*).

Commercial quantities of 95- to 99-percent-pure boron are produced by passing a mixture of boron trichloride gas and hydrogen over a series of electrically heated graphite rods in a resistor furnace. Layers of boron carbide and elemental boron are deposited on the rods. At the conclusion of a furnace run the boron layers are removed from the rods and the elemental boron is separated from the adherent graphite and boron carbide by sorting. Boron carbide, containing 80 to 90 percent boron, is obtained as a byproduct of the process (*6*, *14*). Relatively large amounts of elemental boron of the same purity can be prepared by a three-step process. First, a crude product is produced from the reduction of boron trioxide with magnesium by thermite reaction. The product is roasted with a fluoride and is subsequently leached with water and acids (*22*).

Another method of producing commercial quantities of 99-percent-pure elemental boron consists of electrolyzing a fused bath of potassium chloride or fluoride, potassium fluoborate, and boron oxide in an electrolytic cell. The cell consists of an externally heated crucible of graphite, which serves as the anode, and a low-carbon iron plate mounted for vertical movement into and out of the bath. Electrolysis of the fused mixture at 650° to 1,000° C deposits high-purity boron of the cathode.

USES

Boron compounds are used extensively in the glass and ceramics industries, where their low melting points and excellent fluxing properties are utilized. These properties also are advantageous in brazing, welding, soldering, and refining.

Borax or boric acid is widely used in soaps, cleansers, and detergents because of its easy solubility in water and excellent water-softening properties. Its mild alkalinity in water and its germicidal properties make it useful in toothpaste, mouthwash, and eyewash. Water solutions of borax are used in dyeing leather and textiles, in cleansing hides and skins, in plasters and paints, to prevent mildew and give high gloss to starches, and to prevent mold on leather, textiles, and citrus fruits. In agriculture, borax is added to fertilizers to supply boron as an essential plant nutrient. Boron compounds are also used to control weeds.

Boron compounds are added to alloy steels to increase hardenability. Some elemental boron is used as a deoxidizer in nonferrous metallurgical reactions, as a grain refiner in aluminum, as a thermal neutron absorber in atomic reactors, in delayed action fuses, as an ignitor in radio tubes, and as a coating material in solar batteries.

Compounds of boron such as boron carbide, titanium boride, and tungsten boride are among the hardest substances known. Boron carbide is used in the manufacture of abrasion-resistant parts of spray nozzles, bearing liners, and furnace parts; in the atomic energy field as nuclear reactor control elements and radiation shields; and as an abrasive for ultrasonic grinding and drilling. Boron nitride is useful as a thermal insulator and as a mold lubricant in glass manufacture. Titanium boride is available in commercial quantities but its use is not widespread.

Increasing use is being made of boron trichloride as a catalyst in silicone production, as a synthesis intermediate, and as an extinguishing agent for magnesium fires. Boron trifluoride is used as a catalyst for many organic reactions such as polymerizations, esterifications, and alkylations.

Organic boron compounds such as borate esters are finding greater use as dehydrating agents, synthesis intermediates, special solvents, sources of boron for catalysts, plasticizers, and adhesion additives for latex paint, and fire retardants in plastics and protective coatings. An organic boron compound is used as a motor fuel additive to suppress preignition firing.

Boron compounds such as diborane (B_2H_6), pentaborane (B_5H_9), decaborane ($B_{10}H_{14}$), and alkyl boranes are potential jet and rocket fuels.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

American Potash and West End Chemical obtain a number of coproducts or byproducts at their borax operations. Soda ash, salt cake, potash, sodium chloride, bromine, and lithium compounds are extracted from the Searles Lake brine.

ALTERNATE MATERIALS

There are few substitutes for boron minerals and compounds, inasmuch as they are inexpensive and plentiful. Soda ash and detergents are used as alternate materials in cleaning products.

RESERVES

Estimates were made with due consideration for anticipated increased production rates of the reserves of boron minerals available in the two major domestic sources. These reserves can supply the needs of the industry for more than a hundred years. Measured and indicated reserves of the sodium borate deposit at Boron, Calif., contain over 100 million tons of borax. Indicated reserves of the borax content in the brines and crystalline beds of the Searles Lake deposit total about 150 million tons. In addition to the reserves of the major deposits, the minor deposits of sodium borate could supply an appreciable tonnage of borax.

As production from the domestic deposits of bedded calcium borate practically ceased in 1927, very little exploration has been done since that date to determine the resource potential of these deposits. Some of the deposits are extensive and probably contain appreciable tonnages.

In South America borate deposits occur in Argentina, Chile, Bolivia, and Peru. All of the deposits are primarily sodium borates, except for one bedded deposit in Argentina where the principal ores are calcium borates. Millions of tons of reserves have been reported for the borate deposits, but no data have been published to substantiate these claims.

The measured and indicated reserve of the borate deposits, primarily colemanite, occurring in Turkey is 15 to 20 million tons. Continuing exploration over the past few years indicates that the deposits are extensive, and the potential resource could be substantially larger than the reserve.

Reserves of boric acid occurring in the steam erupting from hot springs at Tuscany, Italy, are difficult to determine because of the nature of the deposit and the uncertainty of the boron source.

The Stassfurt-type deposits of West Germany have small reserves of magnesium borate minerals.

CONSERVATION PRACTICES

Boron mineral producers are adopting conservation practices to lower costs and extend the life of deposits. Conversion of Pacific Coast Borax's mine from underground to open-pit mining methods and the adoption of new procedures for concentrating the ore will permit the mining of larger quantities and the utilization of lower grades of ore. American Potash is employing a new process that produces boric acid from weak brines which cannot be used in conventional processes. Potassium sulfate and sodium sulfate also are produced by the new process.

SOURCES OF STATISTICAL INFORMATION

The Bureau of Mines annually collects and publishes figures on the quantity of boron minerals and compounds sold or used by U.S. producers. The Bureau also compiles figures on imports and exports of boron minerals and compounds from data accumulated by the Bureau of the Census, U.S. Department of Commerce. Information on world production is also obtained from Foreign Service dispatches sent to the U.S. Department of State by its emissaries in foreign countries.

PRODUCTION, CONSUMPTION, AND TRADE

The United States produces more than 85 percent of the world output of boron minerals. Production of boron minerals and compounds (as measured by sales) is shown in table 1. American Potash completed a 35-percent increase in its production capacity in 1962.

Production of boron minerals in Turkey during 1963 totaled 97,100 tons. Most of the Turkish exports are shipped to European markets. In 1963 Italy produced 567 tons of boric acid. Argentina produced 26,691 tons of borax of which 5,500 tons were exported, mainly to Brazil. Production of ulexite in Chile in 1963 totaled 3,286 tons.

Almost half of U.S. production of boron minerals and compounds is exported. In 1963 West Germany, the United Kingdom, France, Japan, Canada, and the Netherlands received the greater part of boron exports; more than 50 other countries received substantial shipments. Imports of boron commodities into the United States are very small and usually consist of special compounds.

TABLE 1.—*Salient boron minerals and compounds statistics in the United States*

	1954–58 (average)	1959	1960	1961	1962	1963
Sold or used by producers:						
Short tons:						
Gross weight [1]	585, 269	619, 946	640, 591	602, 613	646, 613	700, 183
Boron oxide	255, 891	314, 286	323, 955	313, 104	339, 060	369, 302
Value—thousands	$33, 321	$46, 150	$47, 550	$46, 936	$49, 336	$54, 981
Imports for consumption:						
Short tons	[2] 1, 066	91	74	15	15	17
Value—thousands	$148	$174	$202	$52	$51	$58
Exports:						
Short tons	224, 402	253, 674	300, 606	269, 271	292, 264	338, 912
Value—thousands	$15, 660	$21, 047	$25, 576	$23, 212	$24, 736	$27, 519
Consumption, apparent: Short tons	361, 933	366, 363	349, 059	333, 357	354, 364	361, 288

[1] In 1954 gross weight reported included a higher proportion of crude ore to finished products than in 1955–63.
[2] Imports for 1957 include a higher proportion of crude ore to refined products.

According to the Tariff Schedules of the United States (TSUS) which went into effect on August 31, 1963, crude or unmanufactured borax, borate of lime, borate of soda, and other crude and unmanufactured borate materials are free of import duties. Refined sodium borate or borax has an import duty of one-eighth of a cent per pound. Boric acid carries a rate of 5 cents per pound. Boron carbide is rated at 6.25 percent ad valorem. Ferroboron and manganese borate are rated at 10 percent ad valorem. Only small quantities of boron compounds are imported.

STRATEGIC CONSIDERATIONS

In the United States there are large proved reserves of boron minerals, and the possibilities of finding new deposits or extensions of known deposits are good. This country will be self-sufficient for many years at present rates of depletion.

On the other hand, the concentration of the bulk of boron mineral production in a small area approximately 100 to 150 miles from the Pacific coast presents a supply problem in wartime.

GOVERNMENT PROGRAMS

Boron has a great variety of uses important to defense, such as a flux in welding and in brazing, in alloys for cutting tools, and for alloying steel. Export shipments of boron minerals and boron compounds must be licensed. Under the provisions of the Mutual Defense Assistance Act of 1951, boron minerals and compounds were placed under export control because they are items of primary strategic significance used in the production of implements of war. On June 30, 1964, Government inventories totaled 67,636 long dry tons of colemanite in the supplemental stockpile. The ore was acquired by the Commodity Credit Corporation from Turkey in exchange for U.S. surplus agricultural products.

PRICES AND COSTS

A century ago, refined borax was imported from England at a cost of approximately $1 per pound. From 1864 to 1868 an average of 300 tons per year of refined borax was produced in the United States and sold for 28 to 35 cents per pound. In 1874 the price of refined borax in San Francisco, Calif., dropped from an average of 25 cents per pound to as little as 6.5 cents per pound, although the price rose later to between 11 and 13 cents per pound. Since that time it has declined, owing to the discovery and development of deposits of higher grade minerals.

Borax prices at works have remained stable since 1959. Anhydrous boric acid has held at $335 per short ton in carlot quantities, technical-grade anhydrous borax (99 percent) at $92 per ton in bags and $83 per ton in bulk, and technical-grade granular decahydrate borax (95.5 percent) at $50 per ton in bags, or 2.5 cents per pound, and $43.50 per ton in bulk. Warehouse price in New York for decahydrate borax has been reduced from $103.75 (1959 price) to $95 per ton because of reduced freight rates. Quoted price of borax and some boron compounds is published weekly in the Oil, Paint and Drug Reporter.

In 1963, sodium tetraborate pentahydrate sold for $47.50 per short ton in bulk lots, at works, sodium metaborate tetrahydrate, $104.50; sodium metaborate dihydrate, $155; anhydrous borax, $83; ammonium diborate, $303; and ammonium pentaborate, $196.

During 1963 company brochures listed elemental amorphous boron of 90 to 92 percent

purity at $13 per pound in ton lots and $30 per pound in small lots. The price of high-purity, 99-plus percent boron was listed in the American Metal Market as $70 per pound.

Prices of boron carbide and boron nitride products depend on the quantities and grit size distribution. Fabricated products of these compounds are considerably more expensive.

TAXES

Under the Federal income tax law, boron mineral producers have a percentage depletion allowance of 15 percent of gross income, not to exceed 50 percent of the net income without depletion deduction. Kern County, Calif., levies a production tax on boron minerals based on the value of the tonnage mined. A corporation income tax on net income derived from sources within the State is levied by California.

TRANSPORTATION

As boron minerals are bulk commodities, transportation is a critical factor in distribution and price trends. Boron minerals must be transported for long distances from the production areas in southern California to manufacturing areas in the Eastern United States. In November 1963 the first bulk shipment of borate products was made to Europe.

RESEARCH

Industry and Government have a number of research programs on boron and boron compounds. The Bureau of Mines has done research on hard carbides and borides which involved studies of the production and properties of boron carbides and metal borides and on boron mineral mining problems. Currently the Bureau is studying methods of producing ultrapure boron and determining its properties.

U.S. Borax Research Corp., Anaheim, Calif., a subsidiary of United States Borax & Chemical Corp., and the research laboratories of American Potash and Stauffer Chemical are conducting short-term and long-term projects on research and development programs. Emphasis of these programs is placed on the development of titanium diboride electrodes for use in aluminum manufacture, new organic herbicides and problems caused by Federal regulations pertaining to herbicides, development of boron containing inorganic polymers, boric acid esters, boron hydrides, boron-based epoxy resin curing agents, and diboron compounds. Government-sponsored research programs in several fields of boron chemistry were pursued.

General Electric Co., Lockheed Aircraft Corp., Aerojet-General Corp., General Technologies Corp., and several small companies are engaged in experimental work in the boron-filament and composite structures field. An epoxy-boron fiber was developed by the Air Force Systems Command. The U.S. Navy and the National Aeronautics and Space Administration are sponsoring research on the use of boron in structures.

Research leaders in glass fiber industry are concentrating on developing superior properties in glass-fiber textiles and hollow fibers. The glass wool industry is directing its research toward new end uses and improved production methods rather than new types of fiber.

OUTLOOK

The short- and long-range outlook for continued expansion of the markets for boron minerals is attested to by the extensive expansion programs for increased production capacity undertaken by the principal domestic producers. Sodium borates from the open pit mine at Boron, Calif., and the brines from Searles Lake will continue to supply the greater portion of boron minerals; however, production of calcium borates, especially colemanite, is expected to increase substantially.

Turkish boron producers will increase mine and plant capacities to keep pace with the steadily increasing exports of colemanite to processing plants in Italy, West Germany, and France. Substantial tonnages of minerals and refined products may be exported to certain Communist nations if long-term agreements now being negotiated are concluded.

Argentina, with significant deposits of borax and an extensive reserve, could increase its export trade of boron minerals with other South American countries provided that the price was lowered enough to make it competitive with U.S. borax.

The domestic consumption of boron products is expected to increase. Construction of additional production facilities and processing plants should increase as expanding and additional markets are developed and as improved and new products become commercially available.

Increasingly larger quantities of boron compounds will be consumed by the still-growing markets of the well-established uses, namely, household and industrial cleaners and the glass and ceramics industries. The growth rate of the production of these items is closely alined

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with the growth rate in population and the consumption of expenditure durables.

Continued use of large quantities of boron in agriculture, herbicides, and boric acid esters can be anticipated. Development of new merchandizing methods should result in an increase in the sale of more boron products in these fields.

Encouraging results achieved from application research indicate that additional markets for boron products can be anticipated. High-boron borosilicate glass and boron phosphide have applications in the electronics industry. Production is expected to start on improved glass fibers for the textile and plastic industries and for tire cords. The use of titanium diboride electrodes in the aluminum industry is especially promising. Epoxy-boron fiber could revolutionize the structural building material used in military and civilian construction.

Two boron products that have recently been made commercially available could develop into large markets. Alkyl borate will prevent scale formation on reheated steel. The properties of high-performance resin, the first commercial boron polymer, are high heat resistance, strength, hardness, and electrical resistivity. It is adaptable for electrical insulation.

Export of boron minerals and compounds has grown faster than domestic consumption during recent years and is expected to remain a major factor in the economy of the U.S. boron industry. Although shipments of Turkish boron minerals to Europe will increase, the well-established markets of the U.S. producers should not be adversely affected. Facilities for the handling of bulk shipments by oceangoing ships from the west coast of the United States should offset the Turkish transportation advantage.

Possible imports of Turkish colemanite to the east coast of the United States may cause some concern to the domestic mineral producers. Manufacturers of fiber glass, fertilizer, and certain types of glass would replace the boric acid used in their production processes with colemanite, if an economical supply could be obtained.

Most research will probably be directed toward the development of new and improved boron products; however, new end uses of boron will receive attention.

PROBLEMS

Problems related to the mining of boron minerals are minor at present. The anticipated large long-term growth in consumption of boron minerals will make it necessary to mine lower grade minerals at greater depths. Numerous technologic problems will arise which could limit the production rate and increase the cost of boron materials.

Relatively high transportation cost, due in part to the bulky nature of the minerals and the remoteness of the mines from markets, limits the distribution and utilization of boron minerals.

Technical research is required to enable calcium borate minerals to become economically competitive with sodium boron minerals.

Concentration of boron mineral production in a relatively small area in the United States presents a wartime supply problem. More exploration is required to determine the scope of additional areas that could be mined in event of a national emergency.

Development of additional domestic markets is required to compensate for any loss of foreign markets.

A deterrent to the development of more uses for boron products is the difficulty of applying data obtained from laboratory experimentation to economical commercial processes.

The production and use of toxic and relatively unstable boron compounds may present health and safety problems.

Export controls on boron minerals create problems to the firms and governments engaged in international trade.

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BROMINE

By William C. Miller [1]

OCEAN water, brines from saline deposits, and oil-well brines give the United States an inexhaustible source of bromine.

This element is a reddish-brown, volatile, toxic, and corrosive liquid at ordinary temperatures. It is widely distributed in the earth's crust in small quantities and occurs chiefly in natural brines, saline deposits, salt lakes and seas, and the ocean. Bromine is recovered as a coproduct. The 1963 domestic production of bromine compounds totaled 239 million pounds and was valued at $49 million. The United States is self-sufficient in bromine. Additional supplies may become available through programs directed toward the production of fresh water from saline waters.

Short-term consumption of bromine will probably increase; however, long-term demand is uncertain owing to technologic changes.

Problems confronting the bromine industry are—the abundance of supply, the uncertain market for ethylene dibromide, need for more diversified markets, the high price of bromine relative to the price of chlorine, and the need for governmental approval and public acceptance of bromine as fumigant and sanitization agents.

BACKGROUND

Bromine was discovered by Antoine-Jérôme Balard, a French chemist, who extracted it from sea-water bitterns. He published his results in 1826. In Heidelberg, Germany, Carl Löwig obtained bromine from Kreuznach salt-spring liquors and published his results in 1829. In the United States, bromine was recovered from natural brines in 1846 at Freeport, Pa., and in Germany it was detected in 1858 in the salt from the Stassfurt deposits.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

The bromine industry began in 1865 with production from the Stassfurt deposits in Germany. In the United States bromine production started in 1867 as a byproduct of salt production in the Pomerory, Ohio-Hartford and Mason, W. Va., district.

The greater portion of U.S. production has been from well brines in Ohio, West Virginia, and Michigan. Since 1897, except for a 20-year period, 1938–57, Michigan has been the leading bromine producer. Bromine was produced in Ohio until 1951 and in West Virginia until 1961. Bromine production experienced its greatest growth after 1922 when its usefulness in a gasoline antiknock mixture was discovered. In 1924 tests aboard the S.S. *Ethyl* demonstrated the feasibility of recovering bromine economically from the sea. A sea-water recovery plant was built at Kure Beach, N.C., in 1934 and was moved in 1946 to Freeport, Tex. From 1939 until 1958 the bulk of U.S. production of bromine was from sea water.

Annual bromine production in the United States was valued at approximately $49 million in 1963. Slightly over 50 percent of the domestic production is from brine wells, about 35 percent from sea water, and the remainder from oil-well brines and saline-lake brines. Substantial expansion recently completed by two producers of bromine from brines should give the industry sufficient capacity for several years to supply the expected increase in markets.

Bromine is recovered from well brines in Michigan by The Dow Chemical Co., the largest domestic producer, at Midland and Ludington; by the Michigan Corp. at St. Louis and Filer City; by Great Lakes Chemical Corp.; and by Morton Chemical Co. at Manistee. Ethyl-Dow

[1] Commodity specialist.

Chemical Co. extracts bromine from sea water at Freeport, Tex., and Inorganic Chemical Division, F.M.C. Corp., produces bromine from sea-water bitterns at Newark, Calif. Bromine is recovered from oil-well brines near El Dorado, Ark., by Michigan Chemical Corp. and Arkansas Chemicals, Inc. American Potash & Chemical Corp. recovers bromine from saline-lake brines at Trona, Calif.

Bromine is recovered from the Stassfurt deposits of Germany as a byproduct of potash production. In Israel, one of the largest bromide plants in the world extracts bromine from the end brine of potash production from the Dead Sea. Bromine is produced in Japan from bitterns of the sea-salt industry and from brine wells on the Ciba Peninsula. Two sea-water plants furnish bromine for the production of ethylene dibromide in Great Britain. In France bromine is extracted from sea water and potash brines. Italy, India, Spain, and Australia also produce some bromine.

DEFINITION OF TERMS, GRADES, SPECIFICATIONS, AND PROPERTIES

Elemental bromine is marketed in a "purified" grade. Specifications for this grade are—specific gravity at 15° to 20° C, not less than 3.1; bromine, not less than 99.7 percent; iodine, none; and chlorine, not more than 0.1 percent.

Potassium bromide is marketed in technical, U.S.P. (U.S. Pharmacopoeia), C.P. (chemically pure), N.F. (National Formulary), and reagent grades. Potassium bromate is sold in pure (not less than 99.5 percent), C.P., U.S.P., and powder grades. Sodium bromide is sold in grades of C.P., U.S.P., crystalline, powder, commercial, pure, and highest purity. Sodium bromate is available in pure, C.P., and reagent (not less than 99.5 percent) grades. Ammonium bromide is sold as technical, pure, C.P., and N.F.

Specifications for the various grades of bromine compounds are—technical bromine, 99.5 percent pure. Chief impurities are chlorine, traces of moisture, and organic matter. Specifications of the U.S. Pharmacopoeia and the American Chemical Society Committee on Analytical Reagents allow 0.3 percent chlorine, 0.05 percent iodine, 0.002 percent sulfur (0.006 percent SO_4), and no more organic matter in 1 ml than will saturate 50 ml of 5-percent sodium hydroxide solution (*6*)[2]. Chemically pure signifies a minimum of impurities but does not imply 100-percent purity.

Bromine is a reddish-brown, volatile liquid. It is very corrosive and attacks the skin and mucus membrane. The toxicity limit for bromine is one part per million parts of air by volume for an 8-hour workday (*8*).

TECHNOLOGY

Bromine is widely distributed in the earth's crust in relatively small quantities. Few natural bromine minerals are known. It accumulates chiefly in the ocean, salt lakes and seas, and other natural brines in the form of bromide ions and in saline deposits as chloro-bromide crystals.

In the United States, bromine is extracted from brines and bitterns by a steaming-out process and from sea water by a blowing-out process. In both processes four essential steps are employed—(1) treatment with chlorine to oxidize the bromide to bromine, (2) removal of bromine vapor from the solution, (3) condensation of bromine vapor or reacted to form a salt or acid, and (4) purification of bromine.

In the steaming-out process the brine is pumped through a heat exchanger into a packed tower. Chlorine introduced into the bottom of the tower forms hydrochloric acid in the brine, reducing hydrolysis of bromine and increasing process efficiency.

When treating sea-water bittern, concentrated sulfuric acid may be added to reduce alkalinity and minimize hydrolysis of bromine.

The brine continues to a second tower constructed of granite or soapstone and filled with ceramic packing. Steam is introduced at the bottom of the tower, and chlorine is introduced at an intermediate point. Ascending chlorine gas mixes with the hot descending brine, oxidizing bromide to bromine. The bromine is carried from the brine by the steam. Bromine vapor, a little chlorine, and water vapor escape from the top of the tower. A hot bromine-free liquor emerges from the bottom of the tower, is neutralized with lime, and then is pumped to waste through a heat exchanger.

Bromine vapor passes from the tower to a condenser and then into a gravity separator. Noncondensable gases, bearing some chlorine and bromine, escaping from the top of the separator, are returned to the chlorinator. Crude bromine flows through a trap in the bottom of the separator to a distilling column. Here halogenated hydrocarbons are removed, and free chlorine and bromine vapors pass from the top of the separator into a reflux condenser for cooling. Chlorine separated in the condenser is returned to the steaming-out tower. The bromine is purified by a recently developed process that combines physical and chemical treatments. This process has increased the purity of commercially available bromine from 99.80 percent to 99.98 percent. About 95 per-

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

cent of the bromine is recovered from the raw brine.

In the blowing-out process sea water is pumped through a rubber-lined pipe to the top of a brick and concrete tower. Two and six-tenths pounds of 10-percent sulfuric acid per ton of sea water is introduced at the base of the pipe to neutralize bicarbonates in the water. This lowers the pH to 3.5, preventing losses of chlorine and bromine by hydrolysis. Chlorine is added at the top of the pipe to free bromine. Air drawn in at the base of the tower passes through wood packing, countercurrent to the descending brine. The air, laden with bromine, passes from the blowing-out tower through an absorbing tower in which halogens are taken up by sulfur dioxide.

Air from the blowing-out tower is mixed with water vapor and sulfur dioxide. The resulting acids are collected and transferred to a steaming-out tower where bromine and chlorine are liberated. The byproduct hydrochloric-sulfuric acid is used for acidification of the raw ocean water (*6*).

Bromine from the steaming-out tower is introduced into a packed reactor for the production of ethylene dibromide. Descending bromine reacts with a rising stream of ethylene gas forming ethylene dibromide with the evolution of heat. The rate of introduction of bromine and ethylene gas is regulated to maintain a temperature in the reaction zone above the boiling point of bromine but below the boiling point of ethylene bromide. The reaction proceeds in a vapor phase while the liquid ethylene bromide formed flows out of the reactor countercurrent to the incoming stream of ethylene gas. Free acids in the ethylene dibromide are neutralized, and the liquor is fractionated in a still to remove small amounts of ethylene chlorobromide.

USES

The unique combination of nonflammability, chemical activity, bactericidal properties, and high specific gravity gives bromine and its compounds diversified uses. Bromine is important in the gasoline, pharmaceutical, sanitation, photographic, and textile chemical industries. It is used for agriculture purposes and in the production of fire-extinguisher, gauge, and hydraulic fluids. Mineral separation, permanent wave preparations, and the synthesis of dyes also employ the use of bromine.

Brominated organic compounds are the largest consumers of bromine. Ethylene dibromide, the chief compound of bromine, is used as a scavenging agent in leaded gasoline antiknock fluid to prevent the deposition of lead in engines. Other uses of ethylene dibromide are as a reagent in the synthesis of dyes and pharmaceutical intermediates, as a sedative, anaesthetic and antispasmodic agent, and as a solvent for gums and waxes. It is increasingly used in fumigation preparations for control of insects and pests in soil and seeds. Methyl bromide, 1,2-dibromo-3-chloropropane, and 1,3-dibromopropane are utilized in the production of fumigants. Ethyl bromide is used as an intermediate in organic synthesis and in the manufacture of dyes, perfumes, and pharmaceuticals, especially barbiturates. Bromotrichloromethane forms noncatalytic additions with olefins to yield flame-resistant polymers. Tetrabromoethane and bromotrifluoroethylene polymer are utilized as dense media in processing ores or separating solid materials. Trimelylene chlorobromide is used as an intermediate for tranquilizer drugs.

Elemental bromine is used as a bleaching and disinfecting agent, as an alytical reagent in the laboratory, as a swimming pool sanitizer, and for synthesis of bromine compounds. It is used in the manufacture of dyes, ink, resins, and leather and rubber products. The military has used bromine in poison and tear gases.

Chlorobromomethane is used as a noncorrosive fire-extinguishing fluid in homes, factories, and warehouses and as a solvent in organic synthesis. Dibromodifluoromethane is utilized as fire extinguisher at missile bases. Tris (2,3-dibromopropyl) phosphate, tetrabromo phthalic anhydride, and tetrabromo bisphenol-A are used as fire retardants in the manufacture of plastics. Tris (1-bromo,3-chlorisopropyl) phosphate is used as a flame retardant in urethane foam and for certain synthetic fibers. Monobromotrifluoromethane is utilized as an extinguishing agent for fuel and electrical fires.

Metal compounds of bromine are used for the production of high-purity metals. Potassium, sodium, and ammonium bromides are used as nerve sedatives in medicinal preparations and for the preparation of silver bromide emulsions used on photographic films, plates, and papers. Ammonium bromide has minor use in process engraving and lithography. Calcium bromide is an excellent dehydrating agent. It serves also as a sedative in pharmaceutical preparations, as an intermediate in the preparation of organic calcium compounds, and in photography.

Lithium bromide is used in air conditioners. Potassium bromate is used in bread to improve the texture and reduce carbohydrate loss and as a neutralizer in permanent wave preparations. Zinc bromide solutions serve as windows in atomic laboratories to hold back gamma radia-

tion. Zinc bromide is used also as an absorbent in humidity control, as a component of nonflammable nitrocellulose compounds, in rayon finishing, and as a catalyst.

Hydrobromic acid is used as an intermediate in other chemical processes.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

At Searles Lake bromine is recovered as a coproduct from brine that also yields soda ash, salt cake, potash, borax, and lithium minerals. Bromine produced in Texas and California from sea water, and in Michigan from brine, is a coproduct of other compounds. Bromine is produced in conjunction with oil production at El Dorado, Ark. In Israel, bromine is extracted from waste liquors of a potash plant. Bromine is extracted as a coproduct of potash production in Germany.

ALTERNATE MATERIALS

The chemical properties of chlorine and iodine are similar to those of bromine, and these materials are sometimes substituted for bromine. Some substitutes for ethylene dibromide-tetraethyl lead antiknock fluid have been introduced, but the use of ethylene dibromide has continued to grow.

The production of very high-octane gasoline by catalytic cracking and reforming methods is costly. A method of raising the octane rating of low-grade gasoline to the level required by today's engines is to add antiknock fluid. Thus, gasoline containing tetraethyl lead and ethylene dibromide antiknock fluid can be substituted for high-octane nonleaded gasoline.

RESERVES

Known quantities of recoverable concentrations of bromine in sea water and brines are sufficient to supply the U.S. requirements indefinitely. In addition to the present commercial extraction process from sea water, a potential yield of 300,000 pounds per year could be realized from a desalination plant producing 1 million gallons per day of fresh water (*11*).

Indicated reserves and potential resources of bromine in brines obtained from saline deposits which underlie large areas of Michigan and from oil-well brines in Arkansas are large; however, no definite assessment has been made of the quantity.

Sea water, brines from closed basins, oil-well brines, and saline deposits furnish all continents with large indicated reserves and potential resources of bromine. The richest known source outside of the United States is the Dead Sea which contains about 56 percent bromine.

SOURCES OF STATISTICAL INFORMATION

The Bureau conducts an annual canvass of primary domestic producers and publishes figures on production of bromine and bromine compounds as measured by sales. Figures on exports and imports of bromine are compiled and published by the Bureau from data supplied by the Bureau of Census. Figures on production of bromine and bromine compounds in various foreign countries are obtained from State Department Dispatches and published in Mineral Trade Notes. An annual summary of prices for bromine and its compounds is compiled and published from data in the Oil, Paint and Drug Reporter.

PRODUCTION, CONSUMPTION, AND TRADE

About 75 percent of the bromine produced in the United States is converted to ethylene dibromide and consumed chiefly in the nation's automobiles. More than 5 percent is utilized in the production of fumigants.

The tariff schedule of the United States imposes the following duties on imports from non-Communist countries: Bromine 10 cents per pound, potassium bromide 4 cents per pound, sodium bromide 10 cents per pound, ethylene dibromide 2.4 cents per pound plus 12 percent ad valorem.

International trade is a relatively minor factor in the bromine industry. In 1963 the United States exported 11 million pounds of bromine and its compounds, valued at $2 million. Imports of special compounds totaled 374,012 pounds valued at $167,615.

STRATEGIC CONSIDERATIONS

Bromine is not on the list of strategic and critical materials. Concentration of the producing industry in two main areas presents a potential emergency supply problem, as bromine and its compounds have a number of important military uses such as in firefighting fluid and poison gases.

PRICES AND COSTS

The price of elemental bromine in 1963 ranged from 21.5 to 33 cents per pound. Purified bromine in cases, carlots, delivered east of the Rocky Mountains, sold for 32 cents per pound and in tanks, carlots, same basis, sold for 21.5 cents per pound.

TABLE 1.—*Bromine and bromine compounds*[1] *sold by primary producers in the United States*

[Thousand pounds and thousand dollars]

	1954–58 (average)	1959	1960	1961	1962	1963
Elemental bromine:						
Gross weight	9,921	12,537	18,878	17,706	23,106	26,248
Bromine content	9,921	12,537	18,878	17,706	23,106	26,248
Value	$2,364	$2,785	$3,892	$3,510	$4,267	$4,443
Bromine compounds:						
Gross weight	210,584	218,901	188,070	194,791	200,866	212,335
Bromine content	177,471	182,946	156,132	163,092	167,641	177,085
Value	$42,302	$48,723	$40,745	$41,007	$42,350	$44,115
Total:						
Gross weight	220,505	231,438	206,948	212,497	223,972	238,583
Bromine content	187,392	195,483	175,010	180,798	190,747	203,333
Value	$44,666	$51,508	$44,637	$44,517	$46,617	$48,558

[1] Bromine content calculated as theoretical bromine content present in compound.

The prices of bromine compounds were quoted as follows: Potassium bromide, 39 to 40 cents per pound; potassium bromate, 49 cents per pound; sodium bromide, 40 cents per pound; ammonium bromide, 44 cents per pound; ethylene dibromide, 30.5 cents per pound; methyl bromide, 62 to 79 cents per pound.

TAXES

Bromine producers (domestic and foreign) are granted a 5-percent depletion allowance under the Federal Income Tax Law. There are no special taxes levied on the bromine industry.

TRANSPORTATION

Bromine is a corrosive liquid and highly toxic. It requires special handling and transportation under paragraph 73–252 of the Interstate Commerce Commission regulations. A white label is necessary for shipments under paragraph 73–407 of the same regulations. Small quantities are shipped in cases of nine 6.5-pound glass bottles with lead caps packed in expanded mica, diatomaceous earth, or other inert absorbents. Larger quantities are shipped in 10-gallon lead-lined steel drums or in special nickel-clad or lead-lined cars (1). Requirements for tank car shipments are listed in paragraph 73–252, section A3 of the regulations.

RESEARCH

Most research by producers is directed toward the development of new markets and the improvement of product quality. Recently, research has been concentrated on organic bromides. The Bureau is conducting research on the use of bromine heavy liquids for the separation of minerals. Ethylene dibromide and tetraethyl lead, used in automobile motors as antiknock fluid, forms volatile lead halides and complex compounds containing lead halides, which are carried by the exhaust into the atmosphere. The specific reactions that occur in the presence of sunlight to produce eye irritation and oxidant substances known as smog and the role of bromine compounds in the formation of smog are not clearly understood. Air-pollution studies involving gasoline-motor exhaust are being conducted by the Bureau at Bartlesville, Okla. Commercial laboratories and companies also are studying these problems.

OUTLOOK

A growth rate of 4 percent is expected in the bromine market for the short-term outlook. This rate is comparable to the anticipated growth rate of 3.9 for personal consumption expenditure-durable such as automobiles and slightly higher than the anticipated growth rate of 3.5 for tetraethyl and tetramethyl leads. Moderate growth is expected in the consumption of elemental bromine, high-purity bromine, methyl bromide, bromochloromethyl hydantion, tris (2,3-dibromoprophy) phosphate, tetrabromo phthalic anhydride, tetrabromo bisphenol-A 1,3-dibromopropane, and hydrobromic acid.

The trend for each major producer to concentrate research, development, and market expansion effort on its own particular bromine products, is expected to continue.

The long-term outlook for the consumption of bromine is not clear; much depends upon the research of the major producers. Use of the turbine automobile engine would contract the dibromide market, and competition from iodine as a sanitization agent for swimming pools could affect the elemental bromine market. However, increased use of brominated compounds as fire-retardant plastics, additional applications of bromine compounds as intermediates in industrial processes, and improved techniques in producing high-purity metals by sublimation of metal bromides will facilitate growth in the industry.

PROBLEMS

The uncertain market for ethylene dibromide as a gasoline additive and a lack of market diversification will necessitate continued research by the industry. Moreover, commercial applications of laboratory data and methods must be adopted.

Development of safer forms and procedures are required before approval by government agencies and public acceptance will be obtained for the use of bromine as a sanitization agent for home swimming pools.

The high cost of bromine relative to the cost of chlorine deters its wider use and increased consumption.

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CADMIUM

By Harold J. Schroeder[1]

CADMIUM is a soft, malleable, silver-white and relatively rare metal. For many years after its discovery in 1817, cadmium had few applications. In 1910 production was about 100,000 pounds, chiefly in Germany. U.S. production began in 1907, and in 1917, 1919 and ensuing years this country was the leading producer. Demand accelerated after 1919, and in 1963 20 countries produced a total of approximately 26 million pounds of cadmium.

Cadmium is largely associated with the extensively mined zinc sulfide mineral, sphalerite. Accordingly, production of cadmium is almost entirely a byproduct from processing zinc-bearing ores, and the producers of cadmium are the principal producers of zinc or zinc pigments. During 1963 in the United States 10 firms produced cadmium from primary sources and 2 other sources.

The United States has dominated world production since 1919, reaching 81 percent of the total in 1947 but thereafter trending downward to 40 percent for 1961–63. A record domestic output of 11.1 million pounds of cadmium was attained in 1962; the 1959–63 average was 10.1 million pounds, representing a recovery of 11.4 pounds of cadmium per ton of slab zinc produced. For the 1959–63 period about 14 percent of the cadmium was derived from imported cadmium flue dust, and the balance principally from domestic and imported zinc concentrates.

The United States is the largest consumer of cadmium, averaging about 11.3 million pounds per year for 1961–63. Foreign trade in cadmium was relatively small prior to 1952 and since then has been quite variable with most years showing a net import figure.

The first substantial use for cadmium was in paint pigments, but after 1919 its leading use was in plating. In 1963 the major uses were in plating, 55 to 60 percent; pigments and compounds, 30 to 35 percent; and alloys, 7 to 10 percent. Compounds have found increasing applications in plastics, nickel-cadmium batteries, and television tubes. Cadmium used in alloying is principally for solders, brazing alloys, and low-melting-point alloys. Small but important applications of cadmium have been developed for uses such as nuclear reactor control rods, radiation detection devices, photoconductive elements, and transistors.

The quoted price of cadmium metal has ranged from $0.90 per pound in 1945, to $2.55 in 1951, $1.36 in 1959, and $3.00 from yearend 1963 through 1964.

Cadmium will probably be used to the extent of its availability and domestic consumption is expected to increase from about 11 million pounds in 1964 to 12 million pounds by 1970. The higher prices established in 1963 should shift the consumption pattern from plating and pigments towards compounds used in plastics, batteries, and television tubes.

BACKGROUND (18, 19)[2]

Cadmium was discovered in 1817 by a German professor of metallurgy, F. Strohmeyer, while investigating impurities in zinc carbonate from the zinc works at Salzgitter. Strohmeyer and other investigators soon discovered that the new element was a minor constituent of most zinc ores and became concentrated in the flue dusts of zinc distillation furnaces. Small quantities of cadmium in the sulfide form were used in paint pigments, but for more than 60 years after its discovery few additional applications were found. In the latter part of the 19th century new uses in plating steel, in low-melting alloys, and in chemical reagents were developed. However, consump-

[1] Commodity specialist.
[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

tion of cadmium did not achieve substantial growth until after 1919, following the work of M. J. Udy on a new cadmium-electroplating process. Improved recovery methods were devised and until recent years productive capacity has generally been in excess of demand for cadmium.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Cadmium is recovered almost entirely as a byproduct during roasting, smelting, or other processing of zinc bearing ores. Accordingly, many producers of zinc or zinc pigments produce primary cadmium as an integral part of their operation and in some cases also by treating residues and flue dusts collected by other zinc producers.

World production reached around 100,000 pounds by 1910 with Germany accounting for about 90 percent of the total. U.S. production began in 1907 with 14,000 pounds produced by the Grasselli Chemical Co., and in 1910 American Smelting & Refining Co. began production at its Globe, Colo., plant. Other firms entered the field and the United States was the leading producer in 1917 when output reached 207,000 pounds. In 1918 the top ranking position reverted to Germany but since 1919 the United States has been the leading cadmium producer and in 1962 achieved a record 11.1 million pounds, 41 percent of the world total. Domestic cadmium metal production from 1907 to 1963 totaled nearly 250 million pounds.

Twenty countries produced cadmium in 1963 with a total output of about 26.3 million pounds. The United States, the U.S.S.R., Canada, Japan, and Belgium, in ranked order, accounted for 81 percent of the total. The geographical source of the ores yielding recoverable cadmium is not recorded, but it is roughly proportional to the mine output of zinc. All of the cadmium produced in Belgium and part produced in the United States and Japan are from imported ores, while Canada exports additional quantities of cadmium contained in zinc concentrate.

Domestic producers of primary metallic cadmium and their plant locations follow: American Smelting & Refining Co. (Corpus Christi, Tex., and Denver, Colo.); American Zinc Co. of Illinois (East St. Louis, Ill.); The Anaconda Co. (Great Falls, Mont.); Blackwell Zinc Co. (Blackwell, Okla.); The Bunker Hill Co. (Kellogg, Idaho); The Eagle-Picher Co. (Galena, Kans.); National Zinc Co., Inc. (Bartlesville, Okla.); The New Jersey Zinc Co. (Dupue, Ill., and Palmerton, Pa.); St. Joseph Lead Co. (Josephtown, Pa.); and Sherwin-Williams Co. (Coffeyville, Kans.). Domestic producers of secondary metallic cadmium are Arkansas Metals Co. (Jonesboro, Ark.) and United Refining & Smelting Co. (Chicago, Ill.).

There are many consumers of cadmium in the United States. A consumer survey by the Bureau of Mines in 1960 gave the following data: (1) Of the 1,526 respondents, representing 74 percent of apparent commercial consumption, approximately 1,400 gave plating as the sole or major use; (2) 809 plants consumed 1,000 pounds or more and accounting for 96 percent of the reported total; and (3) 51 plants consumed in excess of 25,000 pounds and accounted for 46 percent of the total. Of these 51 plants 35 were engaged in plating and represented 25 percent of the reported consumption for plating. Eight plants consumed 86 percent of the cadmium used in alloys, and seven plants consumed 95 percent of that used for pigments and chemicals.

Approximately 58 percent of the cadmium-consuming industry of the United States is in States bordering the Great Lakes. Of these States, Illinois accounts for about 13 percent, New York 11 percent, Ohio 10 percent, Michigan 8 percent, Pennsylvania 8 percent, Indiana 4 percent, Wisconsin 3 percent, and Minnesota 1 percent. New England contains about 14 percent of the consuming industry with Massachusetts accounting for 7 percent and Connecticut for 6 percent. The remaining 28 percent of the consuming industry is distributed among the other States.

The large consumers of cadmium normally receive their supplies directly from the producer or from direct delivery of imports arranged by a metal dealer. The small consumers of cadmium, chiefly the platers, are generally supplied by an intermediate distributor.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Cadmium is a soft, malleable, silver-white metal when freshly cut. On exposure to moist air the luster dulls owing to formation of a thin coat of cadmium oxide. Some of the physical constants of cadmium are (*18*) atomic number, 48; atomic weight, 112.41; density, 8.65 grams per cm^3 at 20° C; melting point, 321° C; and boiling point, 767° C. Cadmium combines readily with many metals and forms an adherent coating on ferrous metals, properties important in its widespread use. Chemically, cadmium is almost always divalent. It reacts with solutions of the halogens to form corresponding halides, is dissolved in most inorganic and some organic acids, and is not soluble in alkalis. The corrosion resistance of cadmium in rural and

marine atmospheres is good but in industrial atmospheres, particularly where sulfurous fumes are present, corrosion is rapid (*20*). Fumes of cadmium and its compounds and solutions of the compounds are quite toxic (*15*).

Cadmium is produced in several forms. Platers prefer cast ball shapes, some chemical and pigment users prefer sticks or flakes, and certain alloyers desire slabs, ingots, or other shapes. Cadmium sponge is consumed by some compound producers, and several of the cadmium metal producers convert the molten metal directly into the oxide.

American Society for Testing and Materials specifications have not been established for cadmium, but in 1962 the society appointed a task group to develop such specifications and substantial work has been done towards that end. Most cadmium produced in recent years has been at least 99.95 percent pure. Allowable limits of specific impurities depend upon the intended use. Platers permit up to 0.05 percent lead and 0.033 percent zinc, while for most other uses maximums allowed are 0.025 percent lead and 0.02 percent zinc. Cadmium used for pigments must be low in thallium, and solder makers cannot use cadmium with even trace amounts of aluminum.

When shipped to consumers, cadmium sponge has a moisture content of about 25 percent packaged in bags and 35 percent packaged in drums. Even with this precaution substantial oxidation occurs and the cadmium contents on a dry analysis basis are typically 86 percent and 92 percent respectively.

Cadmium of 99.999 percent purity or higher is sold, particularly for electronic uses.

TECHNOLOGY

Cadmium is a relatively rare element, with the abundance in the earth's crust estimated at 0.5 gram per ton. Fortunately for recovery purposes much of this is associated with the extensively mined zinc sulfide mineral, sphalerite, and zinc concentrates from sulfide ore deposits contain from trace quantities up to 1.4 percent cadmium. Cadmium occurs with sphalerite as a solid solution, or as a yellow sulfide coating which is the mineral greenockite if in crystalline form and the mineral xanthochroite if amorphous. Upon weathering, the cadmium sulfide is altered to the oxide or to the carbonate (otavite).

Recovery of the cadmium during processing of zinc-bearing ores follows a variety of procedures (*3–4, 12, 14*). Each system is largely based on the fact that the melting and boiling points of cadmium and its compounds are lower than those of zinc and its analogous compounds, and on the easier reduction of cadmium oxide.

During the roasting and sintering of zinc concentrate, cadmium is concentrated in the collected fumes and baghouse dusts. In lead and copper smelters the initial cadmium content of the feed is low and the fumes must be recycled before the concentration reaches bleed-off levels. Cadmium content of fumes can be upgraded by refuming under controlled conditions in a kiln or reverberatory furnace. In the electrolytic method of producing zinc, the roasted concentrate and the collected fumes are taken into solution with sulfuric acid and a copper-cadmium sludge is precipitated by adding zinc dust. The fumes or sludges may contain from 5 to 50 percent cadmium.

One method of recovering the cadmium is to dissolve the fume or sludge in sulfuric acid, remove impurities by chemical means, precipitate a zinc-cadmium sponge by fractional cementation with zinc dust, redissolve the oxidized sponge in sulfuric acid, and selectively electrodeposit a high-grade cadmium on aluminum cathodes. As an alternative, a controlled addition of zinc dust to the cadmium-containing solution results in an incomplete precipitation of nearly pure cadmium sponge which is briquetted and charged to a retort for upgrading by distillation, then remelted and cast into shapes. In either case the spent liquor is recycled through the zinc recovery process to recover the remaining metal values.

A variation of the foregoing procedures is to take the cadmium into solution by treating a water slurry of the fumes or residue with chlorine gas. After filtering and acidifying, the cadmium is recovered from the solution using the zinc dust precipitation and subsequent steps described previously.

Another method is to combine the fume containing cadmium with the roasted zinc concentrate and allow the cadmium to remain with the zinc produced by distillation methods. In refining the zinc by fractional distillation a cadmium-rich fume is collected and is purified by one of the described methods and cast into shapes.

USES

The largest use of cadmium is for plating manufactured items of steel and other materials used in electrical equipment, transportation, hardware fasteners, and various other items. Ease of plating, even deposition, and excellent corrosion resistance in normal atmospheres, marine conditions, and alkalies give cadmium a wide acceptance for this purpose. Most plating is by electro-deposition (*21*) although parts to be subjected to high stresses may be plated by vacuum vapor deposition to reduce hydrogen embrittlement (*13*).

Cadmium sulfide, sulfoselenide, and lithopone are extensively employed for pigments in a color range of yellow, orange, and red. The pigments exhibit exceptional color permanency even under extreme industrial atmospheres. Other cadmium compounds are finding increased applications, such as stearate for vinyl plastics, nitrate for nickel-cadmium batteries, and phosphors for television tubes (7).

Cadmium combines readily with other metals. A series of solders and brazing alloys contain cadmium as an important constituent along with varying quantities of copper, lead, tin, zinc, or silver. Cadmium is alloyed with lead, tin, and bismuth to form a series of low-melting-point alloys. Small amounts of cadmium are sometimes added to copper to improve strength and hardness with little loss in electrical properties. Cadmium-base bearing metals, extensively used during World War II, are now seldom used. Nuclear reactor control rods and containers for uranium alloys have been made from cadmium alloys.

Both nickel-cadmium and silver-cadmium storage batteries have a high energy to weight ratio and rapid discharge and recharge rates, and both function well in low-temperature operation. They have gained popularity in airplanes, earth satellites, missiles, and small portable items such as shavers, flashlights, and tools.

Another small but important application is the use of cadmium sulfide crystals in photovoltaic cells, radiation detection devices, and photosensitive elements.

ALTERNATE MATERIALS

Zinc and chromium-nickel can substitute for cadmium as a plating material to protect iron and steel from corrosion. Tin and bismuth can be used in place of cadmium in low-melting alloys, and many alternate materials are competitive with cadmium for solders and brazing alloys. A similar competitive situation exists in the field of battery and electronic applications. The chromates of lead, zinc, and barium can in some instances replace cadmium yellow as a pigment. Atomic energy cadmium control rods, which limit neutron activity in an atomic pile, can be replaced by boron, hafnium, samarium, europium, and gadolinium.

Despite vulnerability to substitution in virtually every application, there are enough uses for which cadmium has the desired properties, availability, and price to maintain the demand.

RESERVES

Since cadmium production is almost entirely a byproduct of processing zinc-bearing ores, cadmium reserves are a function of zinc reserves. Analysis of selected samples of zinc concentrates shows a range of 0.5 to 0.6 percent in concentrates from Mexico, 0.1 to 0.4 from Canada, 0.17 to 1.38 from Peru, 0.14 to 0.20 from Australia, and 0.15 to 1.29 from the United States. Owing to the wide range of cadmium contents and incompleteness of data for most ore sources, reserves can only be approximated. Based upon calculated zinc reserves and assigned cadmium contents, the world reserve of cadmium in ore is estimated at 900 million pounds. North America is estimated to possess about 43 percent of this total, principally in Canada and the United States. Eastern and Western Europe are estimated to have 30 percent of the total, and Australia, Africa, Asia, and South America have the remaining 27 percent.

Processing the assigned world cadmium reserves by present technologies would recover about 500 million pounds of cadmium, a 20-year supply at the current rate of consumption.

A minor cadmium resource exists in cadmium-bearing scrap materials such as old batteries, low-melting-point alloys, and process residues.

SOURCES OF STATISTICAL INFORMATION

The Bureau of Mines collects data quarterly on production of metal and compounds and on metal stocks at metal producers, compound manufacturers, and metal dealers. Cadmium consumption surveys were conducted in 1955, 1956, and 1960. The Bureau of the Census, U.S. Department of Commerce, disseminates domestic import and export statistics monthly. The American Bureau of Metal Statistics publishes annual production data for U.S. and Canadian companies that release this data.

The British Bureau of Non-Ferrous Metal Statistics publishes production and consumption data for the United Kingdom, Canada, Australia, Italy, Belgium-Luxembourg, and Norway. Minerais et Metaux (Paris) gives similar data for France.

PRODUCTION, CONSUMPTION, AND TRADE

The United States became the leading producer of cadmium in 1917 with an output of 207,000 pounds. By 1925 this quantity had more than doubled, and by 1931 it was more than 10 times greater. By 1939 output was 4.4 million pounds; the average for 1941–45 was 7.8 million pounds. Annual output for 1959–63 averaged 10.1 million pounds, with a record 11.1

million pounds in 1962. The increased cadmium output has resulted largely from increased zinc output and improved recovery of cadmium. In 1939 slab zinc output was 557,000 tons with 7.9 pounds of cadmium recovered per ton of zinc; the average figures for 1959–63 were 904,000 tons and 11.4 pounds.

Production of cadmium in the remainder of the world has increased rapidly so that the U.S. proportion of the total has trended downward from 81 percent in 1947 to 53 percent by 1958 and 40 percent for 1961–63.

In the United States the metal output in 1963 derived from imported cadmium flue dust was approximately 11 percent, compared with an average of about 15 percent for the preceding 5 years. Except for a relatively small quantity recovered from scrap, the balance of metal output was obtained from processing domestic and imported zinc and other base metal concentrates with the foreign source estimated to be the largest item. The main sources of imported zinc concentrates were Mexico, Canada, and Peru.

Apparent consumption, computed from production, net foreign trade, and industry and Government stock changes, averaged about 6.5 million pounds per year between 1945 and 1952 and thereafter trended upward to an average of 11.3 million pounds for 1961–63. A 1960 consumption survey, accounting for 74 percent of apparent consumption, recorded that about 70 percent of the cadmium was used for plating, 21 percent for pigments and other compounds, and 8 percent for alloys including solder. Estimates for 1963 are plating, 55 to 60 percent; pigments and compounds, 30 to 35 percent; and alloys, 7 to 10 percent. The decline for plating is attributed to difficulties platers have had in obtaining adequate supplies and to substitution of competitive materials as the price of cadmium increased. Most of the increase in pigments and compounds is attributed to use of cadmium in production of cadmium stearate, nitrate, and phosphors.

Foreign trade in cadmium was relatively small prior to 1952 and since then has been quite variable, with most years showing a net import figure. In 1956 imports were 3.1 million tons and in 1960 exports were 2.5 million tons; both values are about twice as high as has been recorded for any other year.

The import duty on cadmium metal, as established at the 1947 Geneva Trade Conference is $0.0375 per pound. Cadmium contained in flue dust, ores, and concentrates is duty free.

TABLE 1.—*World production of cadmium metal, by countries*

[Thousand pounds]

Country	1954–58 (average)	1959	1960	1961	1962	1963
North America:						
Canada	1,894	2,160	2,357	1,358	2,605	2,431
Mexico	[1] 14	[2] 133	[2] 179	[2] 104	[2] 63	[3] 17
United States	10,053	8,710	10,445	10,466	11,137	9,990
South America: Peru	51	141	185	232	235	[5] 400
Europe:						
Austria	[4] 18	43	32	42	49	[5] 50
Belgium	1,367	[2] 1,512	[2] 1,583	[2] 1,988	[2] 1,854	[2 5] 2,000
France	345	539	560	560	540	573
Germany, West	657	926	902	952	560	492
Italy	482	552	648	765	546	514
Netherlands [5]	51	88	88	88	88	88
Norway	239	284	243	231	254	243
Poland	545	860	860	880	880	930
Spain	20	14	26	76	133	[5] 130
U.S.S.R. [5]	1,100	3,310	3,750	4,410	4,410	4,850
United Kingdom	282	310	236	217	237	249
Yugoslavia	26	72	84	[5] 88	[5] 88	[5] 88
Asia: Japan	818	1,082	1,252	1,596	1,940	[5] 2,185
Africa:						
Congo (Léopoldville)	621	1,047	1,113	1,168	650	[5] 220
Northern Rhodesia	[4] 94	-------	58	43	37	[5] 40
Oceania: Australia	722	764	672	676	791	818
World total (estimate)	19,400	22,500	25,300	25,900	27,100	26,300

[1] Exports for 1958 only.
[2] Exports.
[3] U.S. imports.
[4] Average for 1956–58.
[5] Estimate.

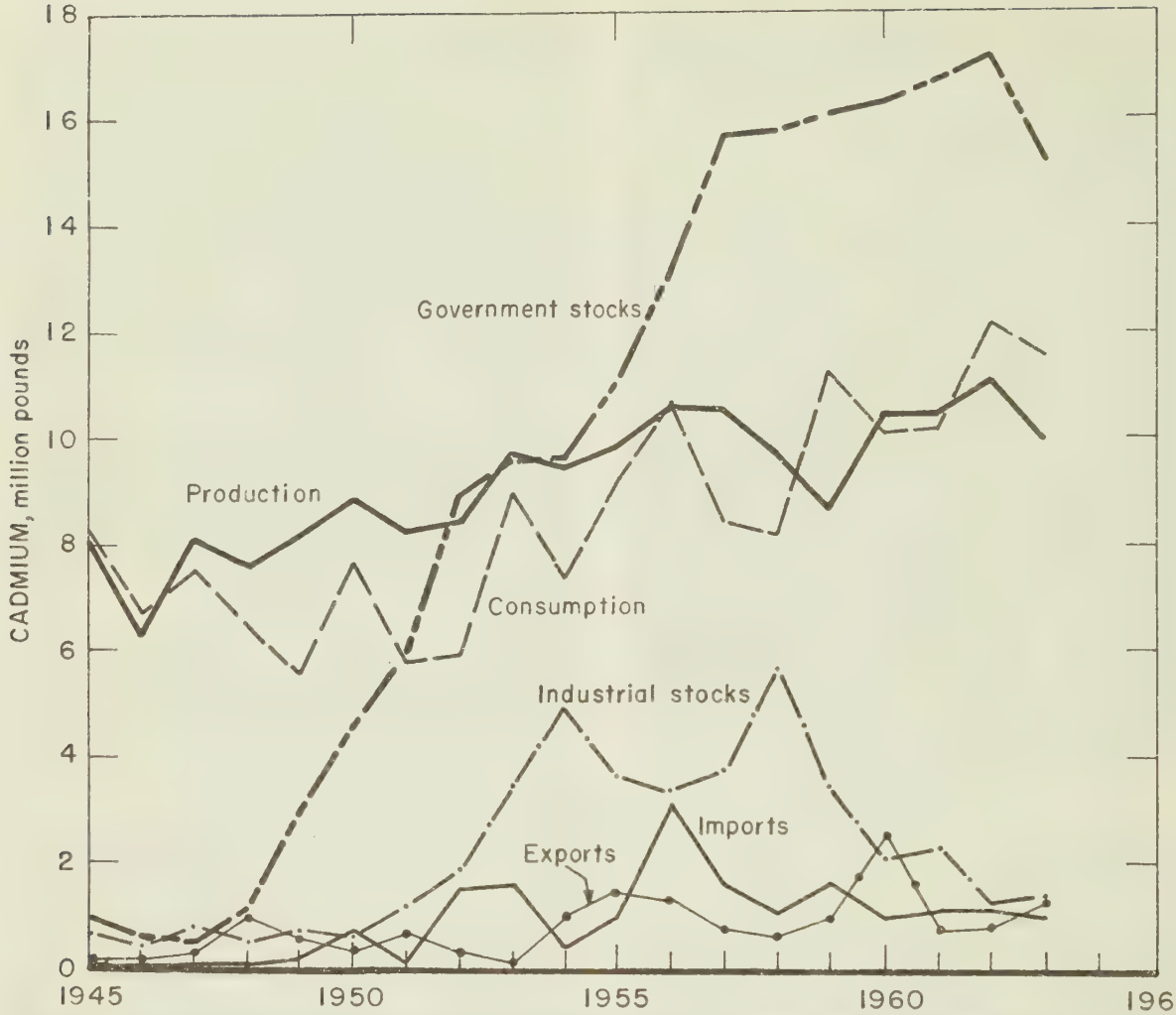

FIGURE 1.—Trends in Production, Commercial Consumption, Yearend Stocks, Imports, and Exports of Cadmium Metal in the United States.

STRATEGIC CONSIDERATIONS

Domestic cadmium metal production formerly exceeded commercial demand, but since 1959 it has fallen short. The source of over half of the recovered cadmium is estimated to be imported cadmium flue dust and zinc concentrates, the bulk coming from Mexico, Canada, and Peru. Canada and Peru also produce substantial quantities of cadmium metal.

Purchase of cadmium under the Strategic Stockpile Act (1946) began in 1948, and buying for the minimum stockpile requirements was completed in 1955. Cadmium was acquired for a supplemental stockpile from 1956 through 1963 under provisions of the Agriculture Trade Development and Assistance Act (1954).

Total inventory of Government stocks increased from 1 million pounds in 1948 to almost 9 million pounds in 1952 and from 9.6 to 15.7 million pounds from 1954 to 1957. At the end of 1962 stocks were 17.2 million pounds, 10.7 million in excess of the 6.5 million pounds announced in March 1962 to be needed for defense. In accord with Public Law 88–8, sales amounting to 2.0 million pounds were made in 1963 from the Government stockpile, reducing the total to 15.2 million pounds on June 30, 1964. Of the total, 7.7 million pounds was in the national (strategic) stockpile, and 7.5 million pounds in the supplemental stockpile. Public Law 88–319, signed by the President on June 12, 1964, authorized disposal of 5.0 million pounds of cadmium, and sales began on July 1, 1964.

PRICES

Cadmium prices have changed substantially since World War II. Quoted producer prices for bars, sticks, and other shapes in lots of 1 to 5 tons, which averaged $0.90 per pound in 1945, advanced for 6 successive years to $2.55 in 1951. Prices declined during the next 8 years to $1.36 for 1959. Thereafter another upward trend occurred and the average for 1963 was $2.26. The price advance during 1963 was from $1.70 to $1.80 at the start of the year to $3.00 at yearend. The $3.00 price was maintained throughout 1964.

RESEARCH

Research relating to discovery, mining, and milling of cadmium is an incidental part of research on zinc or zinc-containing ores. Likewise, much of the research dealing with production of cadmium metal is associated with the larger problems of recovery of the parent base metals. Recovery of cadmium from certain residues, fumes, and other smelter products has been investigated by metal producers (*11*, *24*) and the Bureau of Mines (*5*, *16*, *22*). In recent years research on production has emphasized methods of obtaining high-purity cadmium metal and compounds required for many of the newer uses (*9*, *17*).

The bulk of research on cadmium has been for purposes of utilization. Although plating is one of the oldest uses, a significant amount of research has recently been conducted, particularly with regard to reducing hydrogen embrittlement in plated steel parts subjected to high stress (*2*). Among the methods employed were use of special high-purity plating solutions, heat treatment of the steel part both before and after plating, and use of a vacuum deposition plating procedure. Much research continues on pigments, including development of several cadmium-mercury compounds with improved characteristics for tinting strength, light resistance, and alkali and acid resistance. Other research showed that cadmium compounded with alkyl and aryl phosphites, stearates, and laurates is effective in reducing surface tackiness and controlling age or heat degredation processes occuring in many vinyl resins (*6*).

Perhaps the greatest impetus to research on cadmium in recent years has been the applications of this metal and its compounds in the new fields of electronics, atomic energy, and space exploration (*2*, *8*, *10*, *23*). These investigations have both advanced knowledge of basic properties and explored specific applications. Included in this research are studies by many investigators on characteristics of cadmium compounds for use in transistors, photoconductors, and other functional components in electronic equipment, atomic energy-directed research to use cadmium in control rods for nuclear reactors and container vessels for atomic materials, space-directed research utilizing coated cadmium sulfide crystals for direct conversion of light into electricity, and improvements in nickel-cadmium and silver-cadmium storage batteries.

OUTLOOK

Consumption of cadmium in the United States should rise slowly to about 12 million pounds by 1970. Since in recent years demand has exceeded new supply, the forecast consumption is based on the projected probable availability of cadmium from domestic production, imports, and releases from the national stockpile.

New cadmium supply will continue to be obtained predominately as a byproduct from zinc ores and zinc-bearing lead and copper ores. Cadmium obtained from secondary sources will contribute a minor part of the supply. Hence, output will depend largely upon productivity of zinc smelters, estimated to grow worldwide about 3 percent per year. Domestic zinc smelting is anticipated to exhibit little growth, and imports of Mexican cadmium flue dust, representing a substantial quantity of source material for cadmium production, are forecast to decrease. Some small improvement in recovery of cadmium should offset the reduced quantity of cadmium obtained from flue dust, leaving output from domestic plants substantially at present levels.

Changes in the use pattern of cadmium will continue in adjustment to the large price advances of 1963. Plating will remain the largest single use, although in a few years it will probably decline to about one-half of total consumption. The higher price also promotes substitution of competitive materials for cadmium pigments, and use of cadmium for this purpose will decline from the estimated 15 percent consumed in 1963. Price does not appear to be as great a factor in use of cadmium in solders, low-melting point fusible alloys, and other alloys; consumption for these purposes should remain stable at 7 to 10 percent of total use.

Cadmium compounds, other than those used for colors, represent the most rapidly growing area of use. Consumption of cadmium for this

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purpose is likely to increase substantially from the estimated 15 to 20 percent for 1963. The most important applications will be the stearate for vinyl plastics, the nitrate for nickel-cadmium batteries, and the phosphors for television tubes.

PROBLEMS

A continuing problem to the cadmium producer and consumer is that output depends on base-metal production and thus is virtually unresponsive to changes in demand. An example was the acute shortage of cadmium in 1963 despite knowledge of diminishing stocks and several price advances in the preceding 3 years.

There is a lack of comprehensive knowledge on the geographic source of ore for cadmium production, partly because few ores contain enough cadmium to receive a smelter credit for payment. Thus there are few recorded data on domestic mine production of cadmium or quantities contained in imported ore. With such a poor record of existing output, the estimated reserves and resources of cadmium also are unreliable. The basic facts of occurrence of cadmium in relation to mineral association and genesis of ore deposits are not well enough understood to determine probable concentrations in presently known occurrences or to indicate new sources.

Investigations are needed to delineate problems associated with recovery of cadmium and to develop improved processing methods for reducing the milling and smelting losses. These studies are difficult since the low content of cadmium in the ore requires numerous complex steps in collecting and processing flue dust and residues, making determination of a material balance an involved and costly procedure.

Development of economically sound recovery techniques is required to permit reclamation of the increasing quantities of cadmium now being used in batteries.

A lack of widely accepted specifications for cadmium poses a marketing problem for the producer. There is a general deficiency in the knowledge of limits of impurities that can be tolerated for the different applications of cadmium.

Inadequate statistics on cadmium consumption hinder assessment of trends in usage and projection of requirements.

The toxicity of cadmium fumes requires safeguards during both production and consumption of cadmium and some of its compounds. Cadmium producers also need to take special precautions to prevent poisoning by arsenic which is present in the flue dusts used for plant feed.

The poor corrosion resistance of cadmium to sulfur compounds in industrial atmospheres limits the useful application of cadmium-plated products.

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CARBON

By John W. Cole [1]

CARBON, considered the indispensable element, possesses many physical and chemical properties that make it invaluable to industry. Industrial carbon in this chapter includes all elemental carbon used industrially in applications other than as fuels or reductants, except natural graphites and diamond which are covered in separate chapters.

Industrial carbon is produced by two principal processes from vegetable matter, coal, petroleum and other natural hydrocarbons. In one process the raw material is calcined to drive off volatile matter and leave a high-carbon residue, and in the other, the raw material is partially burned in special combustion chambers and the carbon collected as a deposit or as a precipitate from combustion gases. The industrial carbon produced is not always of sufficient quality for immediate use but may undergo further processing either to remove any remaining impurities or to impart the desirable physical properties required by the end use.

The principal source of raw material for industrial carbon is petroleum and related products. Petroleum coke, a byproduct of thermally cracking various oil stocks in a coking still to yield coke, coker gas oil, and lighter oils and gases, is the preferred material for most uses because of its high-carbon content, low cost, and availability. High-grade petroleum fuel oil, natural gas, and acetylene (to a lesser extent) are used for the production of carbon black. Raw materials such as coal, metallurgical coke, and vegetable or animal materials are used when petroleum coke cannot be processed to produce the desired properties in the end product or when it is more economical to use them.

The United States is self-sufficient in all raw materials for industrial carbon. It has about one-third of the estimated coal reserve of the world, one-ninth of the proved petroleum reserve, and about one-third of the proved natural gas reserve. Reserves of animal and vegetable material are large and renewable.

Carbon is used principally in the manufacture of electrodes, adsorptive materials, chemical compounds, rubber, and pigments. Consumption should keep pace with the growth of the national economy, but current extensive research may find new uses, thereby increasing consumption. Graphites with special properties, such as oriented and recrystallized types, are being developed for use in space-age applications. As more knowledge of them is obtained, their use is expected to grow.

Carbon is not considered a strategic or critical material, probably because the United States is self-sufficient with respect to carbon-containing raw materials. However, carbon is essential for industry to function not only in times of war but also in times of peace.

Problems of the carbon industry are more technologic than economic although new and expanded markets are being sought. The relationship of the raw materials to the properties of the manufactured product, the effective utilization of manufactured carbon and graphite, and the wide range of properties required for end uses are the concern of the carbon industry.

The basic properties of both raw materials and manufactured products need to be studied in detail. In addition, improvements or new processing and manufacturing techniques need to be developed.

BACKGROUND

From the discovery that fire could be tamed to provide comfort and necessities for man, the uses of elemental carbon have ranged from depicting the exploits of cave dwellers, drawn with the charred ends of sticks from the tribal hearth, to its use as an ablative coating on the nose cones of space ships. Forms of elemental carbon range from common charcoal to spun

[1] Commodity specialist.

yarns and woven fabrics with strength and flexibility approaching glass, corrosion and heat resistance superior to metals and ceramics, and electrical resistance that invites its use for heating requirements from the gentle warmth of bed coverings to the white heat of industrial furnaces.

The growth of the carbon industry in the United States, as in the rest of the world, has been tied closely to industrial development. Its great expansion in the United States was triggered in the latter part of the 19th century by the development of the carbon electrode in France. Subsequent research in the utilization of electricity as a source of low-cost power formed the basis for the vast, complex manufactured-carbon industry of today. Carbon aided in the development and growth of the electrical, electrothermic, and electrolytic industries, which in turn resulted in expanded research in carbon utilization with a consequent enormous increase in growth of the carbon industry.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Raw materials used in the production of carbon are petroleum, petroleum coke, natural gas, coal tar pitch, coal, beehive and byproduct coke, gilsonite coke, lignite, peat, nutshells, pulpmill waste, wood, and bone. An analysis of some of the materials is found in table 1.

TABLE 1.—*Range of analyses of carbon materials*

Material	Fixed carbon, percent	Moisture, percent	Volatile matter, percent	Ash, percent	Specific gravity
Coal:					
Anthracite	65. 0–85. 0	2. 4–14. 0	1. 5– 8. 5	6. 0–18. 0	1. 5
Bituminous	49. 0–79. 0	1. 8–19. 0	14. 0–40. 0	2. 8–19. 0	1. 36
Coke:					
Beehive	80. 0–95. 0	. 5– 1. 5	. 3– 3. 0	4. 0–21. 0	1. 9
Byproduct	85. 0–95. 0	. 7– 3. 0	. 6– 3. 3	4. 0–12. 0	1. 9
Petroleum coke	82. 0–97. 0	. 4– 2. 0	4. 0–18. 0	. 5– 2. 0	1. 8
Pitch coke	90. 0–97. 0	. 5– 1. 5	1. 0–15. 0	. 3– 2. 0	1. 6–1. 9
Wood charcoal	84. 0–97. 0	1. 0–10. 0	1. 0–10. 0	1. 0– 4. 0	

During 1963, 34 petroluem refineries in 16 States produced 6.5 million tons of marketable petroleum coke. They are listed in table 2. Marketable petroleum coke, the residue from the distillation of oil, is produced and sold by refiners on long-term contracts to calcining companies or manufacturers of carbon products (*15*).[2] About one-half the petroleum coke sold for industrial use was calcined and used by companies producing primary aluminum. The other half was calcined by four companies at nine plants. Great Lakes Carbon Corp. calcined about three-fourths of the latter amount while the remainder was processed by Union Carbide Corp., Carbon Products Division; R. T. Collier Co.; and Speer Carbon Co., International Graphite & Electrode Division.

Most of the coke produced from coal mined in the United States is used for purposes other than industrial carbon. Approximately 10 percent of the 6,597,399 short tons of coke produced in 1963 by merchant oven- and beehive-coke plants was used for making industrial carbon products, chiefly in calcium-carbide production.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

TABLE 2.—*List of refineries that produced marketable petroleum coke in 1963*

State	Company	Location
Arkansas	American Oil Co	El Dorado.
Delaware	Tidewater Oil Co	Delaware City.
Illinois	Marathon Oil Co	Robinson.
Do	Mobile Oil Co	East St. Louis.
Do	Shell Oil Co	Wood River.
Indiana	American Oil Co	Whiting.
Do	Cities Service Oil Co	East Chicago.
Kansas	CRA, Inc	Coffeeville.
Do	National Coop. Refinery Association.	McPherson.
Louisiana	Continental Oil Co	Lake Charles.
Do	Humble Oil and Refining Co	Baton Rouge.
Michigan	Marathon Oil Co	Detroit.
Do	Mobile Oil Co	Trenton.
Minnesota	Great Northern Oil Co	Pine Bend.
Mississippi	Mississippi Gulf Refining Co	Purvis.
Montana	Humble Oil and Refining Co	Billings.
New Jersey	Mobile Oil Co	Paulsboro.
Ohio	Pure Oil Co	Toledo.
Do	Standard Oil Co. (Ohio), The	Lima.
Do	do	Toledo.
Oklahoma	Cities Service Oil Co	Ponca City.
Do	Continental Oil Co	Do.
Do	D-X Sunray Oil Co	Duncan.
Do	Champlin Oil & Refining Co	Enid.
Texas	La Gloria Oil & Gas Co	Tyler.
Do	Texaco, Inc	Amarillo.
Do	do	El Paso.
Do	American Oil Co	Texas City.
Do	Mobile Oil Co	Beaumont.
Do	Suntide Refining Co	Corpus Christi.
Do	Texaco, Inc	Port Arthur.
Do	Gulf Oil Corp	Do.
Virginia	American Oil Co	Goodwin Neck.
Wyoming	Texaco, Inc	Casper.

Substantial quantities of metallurgical coke suitable for the industrial carbon market were produced in 1963 from Utah gilsonite by the American Gilsonite Co., Gilsonite, Colo.

Raw or semiraw materials used for the production of charcoal and chars ranged from hardwood trees to pulpmill waste and animal bone. In 1960, the latest year for which statistics are available, 1,962 kilns owned by 297 operators produced 328,000 tons of charcoal. Of this amount 235,640 tons was briqueted, presumably for sale as fuel, and the remainder, 92,360 tons, was marketed in bulk. Most of the plants were in the Eastern United States near the principal consumers. Bone char is produced in byproduct plants for distribution to various consumers, principally sugar refiners. The number and location of these plants are unavailable.

Manufactured (artificial) graphite products were produced in 1963 by Union Carbide Corp., Carbon Products Division at Niagara Falls, N.Y., Clarksburg, W. Va., and Lawrenceburg, Tenn.; by Great Lakes Carbon Corp., at Niagara Falls, N.Y., Morgantown, N.C., and Antelope Valley, Calif.; by Speer Carbon Co., International Graphite & Electrode Division, St. Marys, Pa., and Niagara Falls, N.Y.; and by Stackpole Carbon Co., St. Marys, Pa. The Dow Chemical Co., Midland, Mich., produced graphite electrodes for its own use.

The carbon black industry in the United States, the principal world producer, has had a history of migration of the producing areas, steadily increasing demand marked by sudden sustained spurts as major new uses were developed, and abrupt changes in production methods.

Carbon black was undoubtedly produced sporadically in the United States during colonial times, but the first factory was erected at New Cumberland, W. Va., in 1872. The raw material was natural gas; when demand for gas as a fuel forced prices up, the carbon black producers migrated to areas where there was an excess of natural gas. About 1920, Louisiana became the major producing State, but by the end of a decade, Texas became, and remains, the chief producer.

Beginning in 1912, the use of carbon black as an additive to rubber vastly increased consumption; the rising demand, caused by this use, sharply accelerated during World Wars I and II. In 1963, the rubber industry used 94 percent of the carbon black consumed.

During World War II, a furnace process utilizing liquid hydrocarbons was developed that could produce most grades of carbon black. (Some furnace plants also use natural gas.) Up to that time, about 95 percent of the carbon black was produced from natural gas. By 1963, carbon black produced from liquid hydrocarbons amounted to 74 percent of the total U.S. production. Annual output of all kinds of carbon black was over 1 million short tons in 1963. Nine producers in 7 States operated 39 carbon black plants (table 1) with an annual capacity of about 1.2 million tons.

TABLE 3.—*Carbon black producers in the United States, as of Dec. 31, 1963*

State and company	County or parish	Nearest town	Process
Arkansas: Columbian Carbon Co.	Union	El Dorado	Furnace.
California:			
Continental Carbon Co.	Kern	Bakersfield	Do.
Shell Chemical Co.	Contra Costa	Pittsburg	Do.
United Carbon Co.	Kern	Mojave	Do.
Kansas:			
Columbian Carbon Co.	Grand	Hickok	Do.
United Carbon Co., Inc.	do.	Ryus	Do.
Louisiana:			
Cabot Corp.	Evangeline	Ville Platte	Do.
Do.	St. Mary	Franklin	Do.
Columbian Carbon Co.	Avoyelles	Eola	Do.
Do.	Ouachita	Hancock	Do.
Do.	St. Mary	Franklin	Do.
Do.	do.	do.	Channel.
Continental Carbon Co.	Calcasieu	Westlake	Furnace.
Thermatomic Carbon Co.	Ouachita	Monroe	Do.
United Carbon Co., Inc.	St. Mary	Franklin	Do.
New Mexico:			
Continental Carbon Co.	Lea	Eunice	Do.
United Carbon Co., Inc.	do.	do.	Channel.
Oklahoma: Continental Carbon Co.	Kay	Ponca City	Furnace.
Texas:			
Cabot Corp.	Carson	Skellytown	Channel.
Do.	Gray	Pampa	Furnace.
Do.	Howard	Big Spring	Do.
Columbian Carbon Co.	Gaines	Seagraves	Channel.
Do.	Gray	Lefors	Do.
Do.	Montgomery	Conroe	Furnace.
Do.	Terry	Seagraves	Do.
Continental Carbon Co.	Moore	Sunray	Do.
J. M. Huber Corp.	Harris	Baytown	Do.
Do.	Hutchinson	Borger	Do.
Do.	do.	do.	Channel.
Phillips Chemical Co.	do.	do.	Furnace.
Do.	do.	do.	Do.
Do.	do.	do.	Do.
Do.	Orange	Orange	Do.
Sid Richardson Carbon Co.	Ector	Odessa	Channel.
Do.	Howard	Big Spring	Furnace.
United Carbon Co., Inc.	Aransas	Aransas Pass.	Channel.
Do.	do.	do.	Furnace.
Do.	Brooks	Falfurrias	Channel.
Do.	Wheeler	Shamrock	Furnace.

DEFINITION OF TERMS AND GRADES

Industrial carbon, for the purpose of limiting the scope of this chapter, is defined as any elemental carbon used industrially except that used for fuel and reductants and excluding natural graphite and industrial diamond. Carbons used by industry are usually in the form of finished products or materials that contain only minor amounts of impurities, but differ widely in physical characteristics. Terms such as baked, fabricated, amorphous, and manufac-

tured, have been used to qualify carbon in describing articles made by heating extruded or molded raw material to about 1,000° C. When the baking process is carried to higher temperatures (above 2,750° C), the carbon is converted to graphite and the finished product is called manufactured graphite, electrographite, artificial graphite, synthetic graphite, or simply graphite. Herein, it is called manufactured graphite to distinguish it from native or natural graphite.

Many terms used in the finished product segment of the industry are based on the application, such as electrode carbon, projector carbon, or brush carbon. *Green carbon* is coke that has been calcined, ground, mixed with a binder, and pressed into form preparatory to baking into a finished product.

Activated or *active carbon* is an amorphous material produced from coal, or animal and vegetable chars. To activate carbon, it is treated with superheated steam or acids to increase the surface area per unit weight which also increases its adsorption capability. *Bone black* or *bone char* is made by calcining degreased bones in the absence of air and is essentially carbon deposited on a skeleton of tricalcium phosphate.

Coke is a porous, amorphous form of carbon that is the residue of the distillation of volatiles from certain varieties of bituminous coal at high temperatures. The quality of product, that predominantly is used as a reductant for metals or as a metallurgical fuel, is often referred to as metallurgical coke. Coke is graded according to its chemical analysis, its compressive strength, and its resistance to impact and abrasion. The quality of coke is determined by its ash, volatile matter, fixed carbon, and sulfur content. Frequently the composition of the ash also is an important consideration in metallurgical coke.

Petroleum coke, in the form of delayed and fluid coke, is a product of coking processes used in refining petroleum and is the carbon residue left after the production of coker gas oil. *Fluid coke* is used primarily as a fuel. It is a sand-like material composed of small spheroidal particles. *Delayed coke* is the bulk type of petroleum coke discussed here that is used in the manufacture of industrial carbon. Almost pure carbon can be made by calcining petroleum coke above 850° C. Table 4 lists the generally used properties of petroleum coke to be used for anodes in the production of primary aluminum. Petroleum coke for use in the production of silicon carbides should contain neither more than 1 percent sulfur or ash nor less than 9 percent volatile matter. High iron and alumina in the ash are objectionable because they tend to form elemental graphite and silicon metal during the reaction. For use in the production of calcium carbide, petroleum coke should contain less than 2 percent ash, 0.1 percent phosphorus, 1 percent sulfur, and 13 percent volatile material.

TABLE 4.—*Generally used properties of petroleum coke suitable for manufacture of aluminum anodes*

	Green	Calcined
Volatiles, maximum percent	12.0	0.5
Ash, do	0.5 – 1.0	0.5 – .8
Calcium, do	.12	.12
Iron, do	.06	.05– .08
Silicon, do	.06– .08	.05– .08
Sodium, do	.12	.12
Combined Fe-Si, do	.14	.14
Combined Na-Ca, do	.12– .15	.15
Soluble salts, do	.2 – .8	.8
Sulfur, do	1.5 – 2.0	1.0 –2.0
Real density, specific gravity		2.01–2.07

Graphite is an allotropic form of carbon that crystallizes in the hexagonal system. (See "Graphite" chapter.) Diamond also is a crystalline (isometric) allotrope of carbon. (See "Diamond" chapter.)

Pyrolytic graphite, *oriented graphite*, *and recrystallized bulk graphite* are terms used to designate high density, anisotropic, recrystallized manufactured graphite.

Carbon black is a term used to designate a group of nearly pure elementary carbons composed of spherical particles having diameters of 50 to 5,000 angstroms. Their production, physical characteristics, and uses are so different from other carbon materials that they merit special consideration. The pigment trade refers to carbon black from all sources simply as blacks. All carbon blacks, as produced, contain small quantities of hydrogen and oxygen and less than 1 percent ash. They are produced from natural gas, creosote oil, or petroleum fuel oil by partial combustion or thermal decomposition under carefully controlled conditions that determine their particle size, structure, and physical properties.

In the early days of the industry, carbon black was the designation for carbon derived from natural gas, and lampblack was carbon derived from petroleum fluids. Current practice is to designate all blacks as carbon black and to classify them primarily according to method of manufacure and, secondarily, quality. Table 5 shows the most important grades of carbon black in general use, although individual producers have many other brands, grades, and classifications. The two principal methods of manufacture are the channel method, in which small natural gas flames deposit black or soot on steel channels, and the furnace combus-

tion method, in which gaseous and liquid hydrocarbons are incompletely burned in closed retorts and furnaces and the carbon black collected from flue gases. *Channel blacks* are fine-grained, hard, and abrasion-resistant, while *furnace blacks* are soft and flocculent. Special blacks produced by thermal decomposition in preheated furnaces are termed *furnace thermal blacks*. *Acetylene black*, produced from acetylene gas, falls in this category.

TABLE 5.—*Grades of carbon black*

	Main base	Average particle diameter, millimicrons
Channel:		
HCC, high color	Natural gas	5–10
MCC, medium color	do	9–17
LCC, low color	do	17–25
MPC, medium processing (rubber)	do	25–30
EPC, easy processing (rubber)	do	30–33
Furnace (rubber):		
HAF, high abrasion	Oil	33–35
FEF, fast extruding	do	45
HMF, high modulus	Natural gas	55–65
SRF, semireinforcing	do	70–90
Thermal:		
FT, fine	do	150–200
MT, medium	do	250–500
Lampblack	Oil	70–200

Carbon blacks also are graded on the physical properties imparted to the substance to which they are added. About 94 percent of the carbon black produced goes into rubber as a reinforcing agent; the finer the particle size of the blacks the greater is their reinforcing ability. The manufacturing process can be controlled to produce various particle sizes to conform to the degree of reinforcing or abrasion resistance required. For inks and pigments, the degree of blackness is important. Other properties that are important include mass tone, tinting strength, surface area, oil adsorption, organic accelerator absorption, and pH. For certain uses, electrical resistance is an important property.

Technology (*1, 16*)

Carbon occurs in three allotropic forms: Amorphous with a density of 1.8 to 2.1; graphite with a density of 2.25; and diamond with a density of 3.51. Diamond crystallizes in the isometric system, hextetrahedral class, and graphite crystallizes in the dihexagonal-dipyramidal class of the hexagonal system. X-ray studies of amorphous carbon indicate that it also is crystalline although the crystals are too small to be seen with the unaided eye.

Carbon has an atomic number of 6, an atomic weight of 12.010, and six isotopes, C^{10} through C^{15}. Isotopes 12 and 13 are stable; the rest are radioactive with different half lives, the most important of which is C^{14} with a half life of about 5,360 years. The half lives of the other isotopes are a few seconds.

The element has four electrons in its outer shell which may be shared with those of other atoms to form an electron octet. Carbon atoms unite readily with each other or other elements in chains or rings. These compounds form the basis for the science of organic chemistry which lists well over half a million known compounds.

Carbon is inert chemically at room temperature, but oxidizes readily at elevated temperatures. It sublimes at about 3,600° C and boils at about 4,200° C. It is insoluble in all the usual solvents, but dissolves in many molten metals and either separates from them again on cooling or forms carbides with elements more electropositive than carbon.

A high thermal conductivity and a low coefficient of thermal expansion give carbon products a very high resistance to thermal shock. A unique quality among structural materials, carbon is 50 to 75 percent stronger at 4,500° F than at room temperature. It may be formed into shapes either by extruding, molding, or machining. It is a good conductor of electricity.

The geology, occurrence, extraction, and preparation of the mineral source materials, from which carbon is derived, are described in the "Coal," "Diamond," "Graphite," and "Petroleum and Natural Gas" chapters.

The raw materials used in producing industrial carbon, except for certain chars, must be high in fixed carbon and low in ash. The ash-forming constituents must be of the type that can be removed inexpensively. Desirable characteristics found in finished products are not necessarily inherent in the raw materials but may be the result of processing treatment. Most of the raw materials, including coke, are given a preliminary processing by calcination or charring which drives off volatile impurities and results in additional carbonization of hydrocarbons. For some materials, such as bone chars used as adsorbing agents, this initial processing results in a usable product requiring only crushing and sizing. Usually, however, secondary processing is necessary to produce the physical and chemical characteristics required by the particular end use. Processing may include beneficiation, forming, calcination, coking, charring, baking, chemical treatment, or a combination of two or more of these operations. Any or all stages of processing may be done at the raw material source, or by those who process the raw material in bulk form for customers, or by manufacturers of finished products.

Coal

Anthracite and bituminous coal contain ash-forming materials that either are inherent in the coal or extraneous material that is introduced during the mining cycle. To reduce ash-forming materials, the coal is washed, treated by float-sink methods, or upgraded by chemical means. The volatile materials are removed either by preliminary calcination or by baking in the finishing process.

Because bituminous coal is relatively high in volatile matter, its use is limited as a raw material in the production of carbon for many uses. Suitable types of bituminous coal are used to produce coke, which finds extensive use as metallurgical fuel, and to a lesser extent, as a raw material for carbon products.

Anthracite is principally fixed carbon, therefore it is low in volatile matter. Volatile constituents are removed by calcining at about 750° C in closed furnaces in the absence of air. Carbon companies purchase various sizes of anthracite, generally pea through buckwheat No. 4, to insure proper size distribution throughout the electrode or block.

Coke

Coal coke is made by distilling, or coking mixtures of bituminous coals in beehive or byproduct coke ovens.

The beehive oven is a primitive device that derives its name from its shape. It is filled with coal, part of which is allowed to burn with a limited supply of air. All the volatile matter, including gas, ammonia, and tar, escapes through an opening at the top of the oven, where it burns and is wasted.

Byproduct coke ovens are used for large-scale production of coke. Each oven is from 28 to 40 feet long, about 15 feet high, and 14 to 18 inches wide. Heat is supplied by burning gas outside the coking chamber walls. As many as 100 such ovens may be built contiguously in a solid battery. Coal is charged through several holes in the top of each retort, using a car traveling on tracks above the roof of the ovens. A charge consists of 12 to 20 tons of coal depending on the size of the oven.

Coke is produced after heating about 18 hours at about 980° C in the coke bed. Gases leave the chambers through collecting mains and pass successively through processes to recover tar, ammonia, and light oils before passing on to be used as fuel for heating the ovens. Excess gas is used in associated iron and steel plants or distributed through city pipelines to residential and commercial consumers. When coking is complete, the ends of the oven are opened and the red-hot mass of coke is pushed out of the oven by a ram. The ram is mounted on a structure (coke pushing machine) which travels on a set of rails and can be spotted to serve all the ovens in a bank or in several banks. The coke discharges into a special car driven by an electric motor and is transported to a tower where it is quenched with water.

Petroleum coke is produced in special coking units as a byproduct in the thermal cracking of heavy residual oils at 500° to 550° C (*20*). The primary purpose of the operation is to upgrade the residual oil into more valuable light products. The coke as produced contains hydrocarbons and about 95 percent carbon.

Petroleum coke is glossy gray or black, hard, and brittle. For many uses it should be low in sulfur and vanadium and, to facilitate calcining operations, low in chlorides and sulfates. As the final product of distillation processes, petroleum coke contains a concentration of the impurities existing often in trace quantities in the original petroleum. The physical properties of petroleum cokes vary, depending on the crude oil, processing cycles, coking procedure, and crushed particle size and shape.

Calcining companies collect the raw coke from the refineries in bulk form and process the material by firing in kilns for resale as calcined petroleum coke to manufacturers of carbon end products. Although high-purity is required for certain end uses (reactor-grade graphite for example) most calcining companies are not greatly concerned with sulfur and ash content in the raw coke because they can meet the calcined-coke specifications of consumers by blending.

Calcination is done in gas or oil-fired rotary kilns or retorts at about 1,300° C. The main purposes of this firing are to drive off any remaining volatile material and preshrink the coke so that volume changes in subsequent processing will be small and controllable. In addition, electrical and heat conductivities are increased. The calcined coke is then crushed and sized by screening to meet specifications of the consumer.

Charcoal and Chars (*1*)

Organic substances, such as wood and bone, are processed by partial combustion to form charcoal and chars. After carbonization, the material is crushed to size when it is ready for some uses or it may be given special treatment prior to application in other processes.

Both hardwoods and softwoods are used in the production of charcoal. Hardwoods yield hard granular material while the soft resinous woods yield a soft powdery charcoal. The

high-density species of trees yield the most charcoal. Wood carbonization is conducted in beehive kilns, ovens, and continuous retorts at end temperatures between 450° and 500° C. The carbonization time may run from a few days to several weeks.

In the kiln process, the woods are partially ignited under controlled air input conditions to allow only partial combustion. Charcoal yields are 800 to 900 pounds per cord (128 cubic feet) of the heavier woods and 600 to 700 pounds per cord of the lighter softwoods and hardwoods. Charcoal is the only product of kilns. Externally fired ovens and continuous retorts carbonize hardwoods and softwoods yielding charcoal, chemicals (pyroligneous acid), and waste gas. The byproduct carbonizers are equipped with wood predryers and charcoal coolers. The charcoal yield in oven and retort processes is 1,000 to 1,050 pounds per cord from hardwoods and 400 to 450 pounds from resinous woods.

The charcoal produced by these methods is crushed and sized and, depending on end application, is used as such or treated further to obtain physical and chemical characteristics desired in certain end uses. Occasionally, powdery charcoal is pelletized or agglomerated before use; for use in adsorption, it is activated to increase adsorptive characteristics. Activation is done by controlled oxidation with steam or carbon dioxide at 800° to 1,000° C, or with air at 300° to 600° C (*10*). Other activation processes involve heating with minerals and chemicals.

Chars are produced by the carbonization of bone, or dense materials like cocoanut shells or peach pits in horizontal retorts of the byproduct type. Bone is the predominant raw material. Fats, oils, and cartilaginous matter are extracted prior to processing. The bone is charred for 8 hours at about 800° C. The quantity of bone char produced is about 60 percent of the original preextracted charge. The resulting char contains about 75 percent calcium phosphate, 6 percent calcium carbonate, and 10 percent carbon. The carbon is dispersed as a fine film on the skeletonized phosphate and carbonate structure. After carbonization, the char is cooled in the absence of air, crushed, and screened.

Carbon Black

Carbon black is produced by two methods, channel and furnace. The furnace method is the more efficient. The number of channel plants has decreased from 15 in 1960 to 9 in 1963 while the number of furnace plants has increased from 27 to 30. In 1963, the yield of carbon black from natural gas was 4.63 pounds per thousand cubic feet of gas consumed. From hydrocarbon liquids the yield was 4.55 pounds per gallon of liquid feed.

The channel process uses natural gas which, in some cases, is slightly enriched with oil. The gas is burned from specially designed burner tips that produce smokey fan-shaped flames. The flames impinge on long steel channels which move slowly back and forth longitudinally. Carbon black is deposited as a sooty layer on the relatively cool channel, removed by stationary scrapers, and dropped into a hopper from which it is conveyed to storage for market preparation.

The channels and burners are housed in buildings called "burner" or "hot" houses, each containing from 2,000 to 3,500 burners. A carbon black plant may consist of hundreds of houses and hundreds of thousands of flames. Air is introduced at the top and bottom of the houses to control combustion. The different grades of carbon black are produced by changing the feed stock, air intake, burner design, and spacing. Draft, burner tip shape, atmospheric conditions, and kind of fuel are factors that affect quality and productivity.

In the furnace process carbon black is produced by burning hydrocarbon liquids and gases in a refractory-lined furnace at temperatures between 1,100° and 1,650° C. The carbon black produced is carried by hot combustion gases to water spray coolers where the gases are cooled by steps to about 200° C. The gas stream passes through cyclone separators, electric precipitators, and finally bag filters. The cyclones collect about 50 percent, the precipitators 40 percent, and the bag filters 10 percent of the carbon black entrained in the gas stream. The collected carbon black drops into hoppers from which it is conveyed to the packaging and and marketing area.

Acetylene black, one of the carbon blacks, is produced by the thermal decomposition of acetylene (C_2H_2). It was first produced by the channel method. It has been produced by explosive combustion based on the fact that acetylene under pressure of over 2 atmospheres will propagate decomposition through the entire volume if ignited by an electric spark. The most important method of commercial production is to heat acetylene to its decomposition temperature, 800° C. Since the reaction is exothermic, no additional heat is required after the reaction has started.

Acetylene black approaches the properties of finely divided graphite. It has a loose, spongy structure that almost defies compaction. When compressed, it will contract like other carbon

blacks but will soon reexpand when the pressure is released.

The technology of manufacturing graphite is described in the "Graphite" chapter.

Specialized Carbons and Graphites

Outstanding recent advances have been made in the development of high-density carbon and graphite, pyrolytic carbon and graphite, graphite whiskers, and so-called ductile graphite yarn and cloth. Solid carbons, with the exception of diamond, are made up of carbon atoms arranged in a hexagonal molecular pattern in parallel layers. In ordinary or amorphous carbon, the layers are randomly oriented to each other. In graphite the platelets are oriented so that alternate layers of hexagons are offset half the diameter of the hexagon from each other. In pyrolytic carbon and graphite, the individual crystallites are randomly oriented but tend to have their basal planes alined parallel to the surface of deposition. These oriented carbons are electrically and thermally anisotropic, and their conductivities may be almost 1,000 times greater along the layered planes than across them. Pyrolytic graphite is stronger, harder, denser and less permeable than ordinary graphite.

The oriented carbons are produced by the pyrolysis of a hydrocarbon gas. A base material is heated electrically above 1000° C and possibly as high as 2800° C in an evacuated chamber. Hydrocarbon gas is admitted at a constant flow rate. The molecules of gas are decomposed by the heat and the carbon adheres to the base surface.

Carbon yarn and cloth are manufactured by charring synthetic cellulosic filaments in an inert atmosphere after they have been spun and woven into final form (*2*). After charring, the filaments consist of plus 99.5 percent carbon and less than 0.5 percent ash. The tensile strength of the carbon filaments is about 30,000 pounds per square inch.

USES

Consumers of carbon and its products include electrical, automotive, and aviation equipment manufacturers, utility companies, steel, aluminum, and chemical producers; and manufacturers of specialized articles.

Coal and similar substances are used directly as industrial carbon in many applications. Specially prepared anthracite is used as potliner or cathode material for the production of primary aluminum. Anthracite also is used in place of coke in some smelting and carburizing operations. Special uses include battery boxes, granular carbon in telephones, and water filtering. Lignite has been used in the production of activated carbon by Atlas Chemical Co. in Texas, while Pittsburgh Chemical Co., Pittsburgh, Pa., uses bituminous coal for this purpose (*4*).

Coal coke is the principal elemental carbon commodity, and its use as a metallurgical fuel tops all other uses. About 50 million tons is consumed annually by the steel industry alone, where, in addition to being used as a fuel, coke may be classed as a reducing or carburizing agent in the making of steel. Coke fuel is used by other industries and in households for space heating. It also is used for making carburetted water gas, for making carbon bricks for lining furnaces, and for producing calcium carbide.

Petroleum coke probably is the most versatile of the mass-produced carbons, and is widely used because it is a plentiful source of good quality carbon at moderate price. Part of the production is used as a refinery fuel or as commercial fuel, often in powdered form. Its greatest use is as anode material, such as that used in the production of aluminum, and in electric-furnace operations. Another important use is for the production of calcium and silicon carbide. It is the preferred raw material for the production of manufactured graphite, and many types of shapes—block, brick, beams, slabs, and cylinders—are fabricated for use in many industries.

TABLE 6.—*Sales of carbon black for domestic consumption in the United States, by uses*

[Short tons]

Use	1959	1960	1961	1962	1963
Rubber	731,619	681,456	691,446	775,602	815,952
Ink	23,683	23,990	21,493	20,581	23,235
Paint	6,914	6,135	7,633	7,883	6,504
Miscellaneous	3,908	3,228	9,429	15,882	19,018
Total	766,124	714,809	730,001	819,948	864,709

Table 6 shows the average consumption of carbon black in the United States, 1959–63, by major uses.

The use of carbon black in rubber products, where its function is to impart toughness and improve the wearing qualities, far outweighs all others. Applications include tires, shoe soles and heels, hoses, gaskets, and conveyor belts. The average loading of carbon black in rubber, natural and synthetic, amounted to 740 pounds per long ton in 1963.

Carbon black is used as a pigment in inks and paints for newsprint, books, carbons, bags, resins, leather, lacquers, oilcloth and linoleum,

concrete, mortars, stucco, tiles, artificial stones for buildings and jewelry, shoe and stove polishes, and wood finishing. Low bulk, jet-black color, good suspension, ease of grinding, and low oil adsorption are prerequisites for these uses.

Miscellaneous uses include carbon brushes, electrodes, arc carbons, plastics, typewriter ribbons, and many other minor applications.

Activated carbon and chars are used for liquid-phase and vapor-phase adsorption. Liquid-phase adsorptive carbons are used in refining sugar, edible oils and fats, certain foodstuffs, and alcoholic beverages; in processing chemicals and pharmaceuticals; in reclaiming solvents; in recovering adsorbed substances; in purifying water; and as a catalyst. Vapor-phase adsorptive carbons are used for the removal of solvent vapors, odors, and other impurities in air and gases. Most of the bone char production is used to purify cane sugar solutions. After saturation with impurities, the bone char is washed free of sugar and recalcined at about 500° C with restricted air, which destroys the impurities and restores the absorbing power of the carbon.

Manufactured carbon and graphite products include electrodes, anodes, arc carbons, structural and speciality carbons, and brushes for electric generators and motors. Metallurgical applications include furnace linings, trough and tank liners, mold plugs, stool inserts, fluxing tubes, casting molds, sintering boats and trays, and crucibles for induction and arc melting (*13*). Some other industrial uses are welding products, impervious pipe, fittings, valves, pumps, towers, heat exchangers, and tubes. Lubricants, greases, fabrics, piston rings, switch and circuit breaker contacts, anodes and grids for electronic devices, thrust rings for automobile clutches, and moderating material in reactors are among the many special uses.

Carbon also is used in the manufacture of chemical compounds, activated carbon, and manufactured carbon and graphite articles. Chemical compounds are principally carbon disulfide, the carbides of calcium, boron, and silicon, and pigments and dyes. Carbon disulfide is used primarily as a solvent in the vulcanization of rubber and the manufacture of viscose silk or rayon; and in the manufacture of carbon tetrachloride. Calcium carbide is used in the fixation of atmospheric nitrogen and in the production of acetylene (for use as a chemical raw material and in steel-cutting and welding torches). Silicon carbide is used as an abrasive, in crucibles, as resistor rods, and as a superrefractory. Boron carbide is used principally as an abrasive.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Coal, when coked, produces about 10,000 cubic feet of valuable gas per ton of coal. The gas has a heating value of about 550 Btu per cubic foot. The principal use for coke is in the steel industry, but it is also important in smelting of nonferrous metals. Water gas, produced from coke and enriched with gases from cracked oil (called carburetted water gas) has served as fuel for residential and industrial consumers. Water gas may be used also for the synthesis of motor fuels, methanol, and other chemicals.

Ammonia, coal tar, and light oils are important byproducts of coke production. Ammonia is used for chemicals and fertilizers. Coal tar is a mixture of many organic chemical compounds which have formed the basis of the aniline and dye industries. The light oils consist of benzene, toluene, xylene, and naphtha, which are the raw materials used for the production of many organic chemicals.

Petroleum coke is a byproduct of coking processes in the cracking of petroleum stocks—usually residual oils. The primary purpose of the process is the production of coker gas oil which can be charged to catalytic or thermal crackers for producing lower boiling fuels, principally gasoline. All petroleum refining processes do not produce petroleum coke, particularly those that produce residual fuels and lubricating oils as an end product.

Carbon black was once produced almost entirely from sour natural gas, which had no other market. Today, the major part of domestic carbon black is made from liquid petroleum fractions.

ALTERNATE MATERIALS

There are no satisfactory substitutes for carbon in its major applications. Manufactured and natural graphite vie with each other in many uses, but the manufactured variety is unsuited for some uses, especially where large natural flake is required as in graphite crucibles. For use in nuclear reactors, manufactured graphite is preferred because of its greater purity and because it can be formed more easily into special shapes.

Silica gel, fuller's earth, activated clay, and activated alumina are used in place of activated charcoal and chars in some types of liquid- and gas-phase adsorption. Carbon may be displaced if the other materials prove to be more suited for the removal of a particular impurity. However, changes in established adsorption systems or adsorbents in the principal applica-

tions are slow to develop even though a new material may prove to be more efficient.

RESERVES

Industrial carbon can be produced from coal, petroleum, other mineral hydrocarbons, and many vegetative materials. Reserves, both foreign and domestic, are large and in the case of vegetable material such as trees, they are replaceable and thus incalculable. The United States has about one-third of the estimated coal reserve of the world, one-ninth of the proved petroleum reserve, and about one-third of the proved gas reserve. Data on fossil fuel reserves are shown in chapters on the fuel minerals.

SOURCES OF STATISTICAL INFORMATION

Annual data on the quantity and value of production and sales of petroleum coke, metallurgical coke, coal and lignite, natural gas, and carbon black are obtained by canvass of domestic producers and published by the Bureau of Mines. Additional information is available from the Departments of Labor and Commerce, the Federal Power Commission, the Interstate Commerce Commission, and State mining agencies, in addition to sales agents, dealers, distributors, railroads, traffic associations, and consumers. Much information is available from publications of the Petroleum Institute, the American Gas Association, and the American Carbon Committee. With the exception of raw materials for carbon black no breakdown is given for quantities used as industrial carbon. No canvass of users is made.

World production and trade data are compiled from data collected by the U.S. Department of State and U.S. exports and imports are compiled from data supplied by the U.S. Department of Commerce.

PRODUCTION, CONSUMPTION, AND TRADE

Data on the production and consumption of carbon for all industrial uses are not published as such. Published production and consumption data on the major raw materials—coal, coke, and charcoal—include uses other than industrial carbon. Table 7 gives estimated consumption of carbon by uses in the United States in 1963. The data on silicon carbide, calcium carbide, and carbon disulfide were estimated from the quantity of carbon materials required to manufacture the quantity of these chemical compounds produced in the United States. The estimates on anodes and electrodes were published in the trade journals. Data on carbon black were published by the Bureau of Mines and the data on activated carbon and chars were obtained from the Bureau of the Census.

TABLE 7.—*Estimated consumption of industrial carbon in the United States in 1963, by major uses*

[Short tons]

Carbon containing product	Carbon used in manufacture
Electrodes:	
Anodes (for aluminum production)	1,500,000
Cathodes (for aluminum production)	100,000
Other electrodes	590,000
Carbon black:	
Rubber	815,000
Ink	23,000
Paint	6,500
Miscellaneous	19,000
Silicon carbide	60,000
Calcium carbide	416,000
Carbon disulfide	41,000
Activated carbon	72,000
Bone chars	11,500
Miscellaneous	170,000
Total	3,824,000

Data on world production and consumption of industrial carbon are not available and data on U.S. imports and exports are not completely reliable. Imports are generally small, and known exports consist chiefly of carbon black, petroleum coke, and anthracite coal. A trade journal estimated that 250,000 tons of petroleum coke per year is exported to Canada for use in the production of primary aluminum (*17*). It is estimated that 150,000 tons of anthracite per year is exported to Canada for use as cathodes in the production of aluminum.

Production and shipments of carbon black in the United States in 1963 by grades are shown in table 8, and the production by States and districts is shown in table 9.

TABLE 8.—*Production and shipments of carbon black in the United States in 1963, by grades*

[Thousand pounds]

	Production	Shipments (Including exports)
Furnace:		
Semireinforcing	299,986	306,684
High-modulus	53,137	57,293
General-purpose	175,197	179,297
Fast-extrusion	237,419	242,579
High-abrasion	502,138	510,232
Superabrasive	11,927	16,343
Intermediate-abrasion	406,506	415,489
Thermal	193,594	200,850
Total	1,879,904	1,928,767
Channel	179,012	170,173
Total	2,058,916	2,098,940

TABLE 9.—*Carbon black produced in the United States, 1960, by States and districts*

State or district	Producers reporting [1]	Number of plants	Production					
			Furnace black			Channel black		
			Thousand pounds	Value at plant		Thousand pounds	Value at plant	
				Total (thousands)	Cents per pound		Total (thousands)	Cents per pound
Louisiana	6	9	631, 488	$42, 263	6. 69	(2)	(2)	(2)
Texas:								
Panhandle district	7	12	482, 738	33, 234	6. 88	78, 381	$11, 146	14. 22
Rest of State	6	12	396, 231	28, 718	7. 25	127, 506	11, 060	8. 67
Total	8	24	878, 969	61, 952	7. 05	205, 887	22, 206	10. 79
Arkansas	1	1	227, 001	15, 831	6. 97	----------	----------	---------
Oklahoma	1	1						
California	1	1						
Kansas	2	2						
New Mexico	3	4	23, 847	1, 168	4. 90	86, 535	7, 354	8. 50
Grand total	11	42	1, 761, 305	121, 214	6. 88	292, 422	29, 560	10. 11

[1] Detail will not add to totals because some producers operated in more than 1 area.
[2] Included with "Texas: Rest of State" to avoid disclosure of individual company confidential data.

World production of carbon black was not known in 1963. Known producers were United States, United Kingdom, West Germany, Rumania, Japan, Brazil, France, Yugoslavia, Canada, China, and Italy. The first three were the leading producers. The rising demand for rubber in foreign countries has increased demand for carbon black (*5*). This demand has been met in the past by exports from the United States, but in recent years, the number of carbon black plants in foreign countries has been rising. The loss in U.S. exports is partially offset by the fact that almost all of the new foreign plants are financed with American capital.

Charcoal and chars were imported from Mexico, Japan, Canada, Ceylon, United Kingdom, Netherlands, Egypt, Portugal, France, and Jamaica. Carbon black was imported principally from Canada with small quantities coming from West Germany, United Kingdom, Switzerland, Netherlands, and Japan.

Charcoal and chars were exported to 55 countries, principally Mexico, Canada, Argentina, Brazil, Venezuela, France, Italy, West Germany, Belgium-Luxembourg, United Kingdom, Sweden, Japan, India, Republic of South Africa, and Australia. Carbon black was exported to over 45 countries on 6 continents shown summarized in table 10.

Ad valorem tariff rates effective in 1963 were bone black and bone char, 20 percent; artificial graphite, 5 percent; calcined petroleum coke, 15 percent; carbons and chars, activated or not, 19 percent; acetylene black, 5 percent; gas black pigments, 5 percent; and liquid black pigment, 10 percent.

TABLE 10.—*Carbon black exported from the United States in 1963*

[Thousand pounds and thousand dollars]

	Quantity	Value
North America	49, 742	$4, 154
South America	38, 624	3, 444
Europe	178, 936	17, 845
Asia	75, 203	7, 261
Africa	18, 434	1, 796
Oceania	9, 989	947
Total	370, 928	35, 447

STRATEGIC CONSIDERATIONS

The United States is self-sufficient in all forms of carbon raw material. The supply of coal and woody materials is virtually unlimited and the supply of petroleum and natural gas, although more limited than the others, is adequate.

Present production and need for petroleum coke as a raw material for industrial carbon is below actual or potential capacity. Many refineries do not produce marketable coke either because they do not have coking facilities or because there is no readily available market. The increasing use of petroleum liquids in the production of carbon black makes that portion of the carbon industry subject to any wartime shortage in the petroleum industry. Natural gas, the other source of carbon black, is not affected by wartime demands to the extent that petroleum is. A loss in carbon black production due to petroleum shortages might be offset by increased production from natural gas.

PRICES

No formal data are published on petroleum coke prices. Prices taken from articles in trade journals range from $10 to $20 per ton and are subject to negotiation by buyer and seller. Prices paid to the petroleum refiner depend on plant location, quality and quantity of the coke, and other factors. In 1963, the average value of coke made from coal was $15.38 per ton.

Prices of carbon black are given in table 11. The average value of natural gas used in the production of carbon black during 1963 was 12.70 cents per thousand cubic feet and the value of liquid hydrocarbons used was 6.66 cents per gallon.

TABLE 11.—*Prices of carbon black in carlots, f.o.b. plant, 1963*

[Cents per pound]

Date	Channel blacks ordinary rubber grades[1]		Furnace blacks (bags)			
	Bags	Bulk	Semi-reinforcing grades	High-modulus grades	Fast-extrusion grades	High-abrasion grades
Jan. 14, 1963	9.25	8.75	5.50	6.00	6.50	7.50
June 3, 1963	9.25	8.75	5.75	6.25	8.75	7.50

[1] Chiefly easy-processing and medium-processing, but also includes hard-processing and conductive channel blacks.

Source: Oil, Paint and Drug Reporter.

TAXES

No special taxes are imposed on the carbon industry, other than those that are applied to the raw materials: Anthracite, coal, petroleum, and natural gas.

RESEARCH

Research on manufactured carbon by government and private industry is directed toward fundamental studies of the physical and chemical properties of carbon, and research to improve present applications and develop new uses.

Research on basic properties has involved kinetics, electron spin resonance, atomic dislocations, surface reactions, catalytic properties, and radiation effects. Research also included the mechanism of carbon formation, high-temperature properties, mechanism and rate of graphitization, heat treatment effects, and electronic properties.

With the exception of special carbons, techniques of manufacturing industrial carbon appear to be fairly stabilized, and most research in this area is directed toward improving present systems utilizing carbon end products. In addition, research is conducted on the carbon product to improve performance or to develop new uses.

Manufactured carbon and graphite have great high-temperature strength, extreme resistance to thermal shock, high thermal conductivity, and relatively low density. These properties have led to its consideration as a material for use in space vehicles. However, heterogeneous physical properties and structure in single specimens coupled with a high rate of oxidation at elevated temperatures have presented problems. Much of the present research is directed toward overcoming these obstacles.

The intense research on the physical and chemical properties of oriented carbon and graphite reflects a desire to use these materials in space applications. The Federal Government, through research contracts with private industry, is conducting extensive research on all types of manufactured carbon and graphite with particular interest on those materials with possible applications in missiles, high-speed aircraft, and space vehicles. A great part of the research and development sponsored by the Government is on the refractory properties of graphite and its possible use at temperatures above 3,000° C.

Government agencies that are conducting noteworthy research on some applications of carbon include the various laboratories of AEC—Argonne, Brookhaven, and Oak Ridge National Laboratories—and the Bureau of Standards.

Firms that have had a major role in the Government program to improve carbon and graphite products, including pyrolytic graphite, are Union Carbide Corp., Carbon Products Division, Lawrenceburg, Tenn.; General Electric Co., Hanford, Wash., and Schenectady, N.Y.; Lockheed Missiles and Space Co., Palo Alto, Calif.; Raytheon Manufacturing Co., Waltham, Mass.; Bell Telephone Laboratories, New York, N.Y.; Atomics International, a division of North American Aviation, Canoga Park Calif.; and Westinghouse Electric Co., Pittsburgh, Pa.

Among other companies that maintain staffs for research on carbon and graphite (and their principal field of research) are the following:

Company and location:	*Field of research*
Stackpole Carbon Co., St. Marys, Pa.	Carbon and graphite uses.
Pure Carbon Co., St. Marys, Pa.	Do.
Atlas Powder Co., Wilmington, Del.	Activated carbons.
Darco Experimental Lab., Marshall, Tex.	Do.

Company and location—Con.	*Field of research*
The Carborundum Co., Niagara Falls, N.Y.	Carbides, Superrefactories.
C. L. Mantell & Asso., New York, N.Y.	Activated carbon, electrodes.
Speer Carbon Co., St. Marys, Pa.	Nuclear and electrode graphite.
Asbury Graphite Mills, Inc., Asbury, N.J.	Blacking and plumbago.
Eagle Pencil Industries, Inc., Danbury, Conn.	Carbon in rubber and pigments.
Columbian Carbon Co., New York, N.Y.	Uses of carbon black.
Great Lakes Carbon Co., New York, N.Y.	Manufactured graphite.
United Carbon Co., Houston, Tex.	Carbon black.
Joseph Dixon Crucible Co., Jersey City, N.J.	Graphite refactories and crucibles.
Acheson Colloids Co., Port Huron, Mich.	Pigment carbon black.

The American Carbon Committee is composed of members who represent university, government, and industrial laboratories which study carbon by physical and chemical methods. The interests of the members encompass manufacture, properties, and use of carbonaceous materials. Publication and discussion of research results are promoted through conferences on carbon convened at 2-year intervals. The Fifth Carbon Conference, convened at Pennsylvania University June 19–23, 1961, resulted in publication of 2 volumes containing 157 papers (*2*).

The Society of Chemical Industry, London, England, is the British counterpart of the American Carbon Committee and periodically holds conferences on the industrial uses of carbon and graphite (*20*).

OUTLOOK

The short- and long-term supply outlook for industrial carbon required by the U.S. domestic economy does not pose any difficult problems. The supply of all types of raw materials is more than adequate and it would take a large increase in consumption to create any shortage in raw materials.

Consumption is not expected to increase greatly but should at least keep pace with the growth of the national economy and may better the gross national product rate. The great amount of current research may develop new uses that could change present consumption trends. This is particularly true of carbon black whose reinforcing properties may have many other applications besides rubber. However, the use of industrial carbon in special applications, such as space vehicles or atomic reactors, is not expected to increase overall consumption greatly. Such uses receive spectacular publicity but they do not involve large quantities of carbon.

Production facilities for all kinds of carbon raw materials are adequate. The expansion of carbon black production plants in foreign countries should cut domestic exports, thereby making domestic plants more than adequate for domestic needs. Furnace methods of producing carbon black will continue to displace the less-efficient channel process. The capacity of manufactured carbon and graphite plants is adequate for present needs.

PROBLEMS

Sources of statistics are inadequate to determine precisely the requirements, supply, resources of industrial carbon, and the quantities and qualities required by different consumers. Ample supplies of raw materials have created a lax situation in the statistical canvassing of the industry.

One of the major problems of the carbon industry is to determine the degree of interchangeability of the various raw materials. Most of the raw materials are used for fuels; often only a small portion of the production is used for industrial carbon. Future demand for some of these materials in other markets may force carbon manufacturers to develop new sources.

A major technologic problem is how to improve recovery of carbon black in the furnace method of manufacture. The operating efficiency for the furnace method is about 50 percent for oil feed and about 20 percent for gas feed.

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CEMENT

By William R. Barton [1]

PORTLAND cement concrete is the most widely used construction material in the world. In the United States, almost twice as much concrete is used as all other structural materials combined.

The United States produces and consumes more than 16 percent of the world's cement. Our economy requires almost 2 barrels (all barrels in this report are 376 pounds each unless otherwise noted) of cement per person with a total 1963 value of $1.2 billion. The portland cement industry in 1963 comprised 181 producing plants in 40 States and Puerto Rico with a total production capacity of 478 million barrels.

A domestic cement industry has become almost a prerequisite in any country where industrialization is undertaken. As result many under-developed nations have established indigenous cement industries. Therefore, while U.S. cement use has consistently increased, it is a decreasing percentage of total World demand.

New production machinery and methods have constantly lowered cement production costs. At the same time, more rigorous specifications for cement and more sophisticated consumer tastes and needs have proliferated the special types of cement on the market. New automated bulk transportation equipment and local market distribution centers permit the industry more flexibility in meeting customer needs.

Continued growth of the cement industry is forecast as population increases generate a need for more highways, schools, dams, housing, and industrial plants. Continued technological innovations will hold the cost of cement at favorable levels in relation with competitive building materials.

BACKGROUND

As early as 2500 B.C., clay was added to lime mortar to make hydraulic cement in the Near East. The word "cement" was first used more than 2,000 years ago by the Romans to describe impure limes used as mortar in stonework. With the decline of the Roman Empire, the secret of cement manufacture was forgotten, and it was 1756 before examination of an ancient Latin manuscript by English engineer John Smeaton, led to the rediscovery of Roman hydraulic cement, which was superior to the straight lime mortars then in general use. The new natural cements soon became popular in England, France, and other European countries. In 1824 Joseph Aspdin, an English bricklayer and stonemason, obtained a patent for making "Portland cement," so called because it resembled stone quarried on the Isle of Portland. Essential improvements in the manufacture of modern portland cement are the scientific blending of raw materials to a uniform composition and the burning to incipient fusion rather than simple calcining as in the case of natural cements. By 1850 portland cement began to displace natural cement in all European markets.

The cement industry in the United States began early in the 19th century when a construction material better than quicklime was needed for masonry work and locks of canals in New York, Pennsylvania, Maryland, Illinois, and Kentucky. Beds of argillaceous limestones in each State were found to possess good hydraulic properties when calcined. Natural cements equal in quality to European cements were made from the limestones and used in constructing the Erie, Chesapeake and Ohio, and many other well known canals. In 1875, the first attempts to produce portland cement in the United States were made at some of the natural cement plants. Throughout the 19th century, natural cement production continued to

[1] Commodity specialist.

grow despite imports of European portland cements and the competition from the struggling portland cement branch of the domestic industry. In the larger cities, brick and stone buildings were erected with natural cement mortars whereas quicklime formerly had been used. In 1899, there were 76 cement plants that produced 10 million barrels of natural cement.

By 1895, production of portland cement had risen to 1 million barrels with 40 percent produced in rotary kilns using oil as a fuel. In 1899, there were 36 plants producing portland cement, and 66 percent of the 6 million barrels produced was from plants using rotary kilns. The successful application of powdered coal as a fuel for rotary kilns gave great impetus to the rise of the portland cement industry. In 1910, the number of portland cement plants had increased to 111, and over 76 million barrels were produced, practically all in rotary kilns.

After 1899, many natural cement plants were converted to portland cement plants, and since 1910 only a few plants have continued to produce natural cements.

From 1910 until 1929 the portland cement industry expanded until there were 88 companies with 168 plants. The depression of 1929 stopped further growth of the portland cement industry for 17 years; 20 companies ceased operation, and 16 others were absorbed by other companies.

After World War II, expansion resumed and by 1954, 75 companies operated 157 plants in the United States. Since that time increasing competition has resulted in numerous consolidations so that while the number of operating plants increased to 181, in 1963, the number of operating companies was reduced to 52. Seven firms operate single plants making natural, slag, or portland-pozzolan cement (5 of these are also included in the list of 52 portland cement companies).

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Cement is produced in many countries throughout the world. Most of the highly industrialized nations export varying quantities of cement to the less developed nations. A domestic cement industry has become almost a prerequisite in any country where industrialization and attendant heavy construction projects are undertaken. As a result, in the past 10 years many of the newly constituted nations have created their own cement industry with the aid of capital investment, loans, or grants from business or governments of highly developed countries.

The United States is the largest single cement producing and consuming country in the world, but owing to rapid rises in overseas demands our share of world production and consumption has declined from more than 20 percent in 1958 to about 16 percent in 1963.

Value of sales at cement plants in the United States was $1.2 billion in 1963, representing one of the largest segments of the Nation's mineral industry. U.S. imports and exports of cement are relatively unimportant, rarely exceeding 2 percent of the domestic production, although locally for short periods imports can severely affect the market.

Of the 52 companies producing portland cement in the United States during 1963, 13 were subsidiaries of or affiliated with firms not engaged primarily in cement manufacture. These 13 subsidiary cement firms comprised 28 percent of U.S. portland cement production capacity. Four of these subsidiaries were among the 10 largest cement companies. In 1963, the 10 largest producing companies owned 57 percent of total U.S. cement capacity, and the 18 largest accounted for 79 percent of the national total.

In addition to the 181 portland cement plants with a total capacity of 478 million barrels, approximately 200 distribution centers were operated by the cement manufacturers for efficient marketing in major domestic consuming centers.

Until 1917, world production of cement was concentrated in a few European countries and the United States. Since then local cement industries have germinated in all parts of the world, and in 1963 production was reported from more than 90 countries in 6 continents.

In the 19th century, the domestic cement industry was concentrated in New York and Pennsylvania, close to the large population centers. As the country grew and construction requirements spread to other sections of the Nation, the cement industry expanded into other States. In 1963, there were 181 producing portland cement plants in 40 States and Puerto Rico. Only Alaska, Nevada, North Dakota, the District of Columbia, Delaware, New Jersey, Connecticut, Rhode Island, Massachussets, Vermont, and New Hampshire did not have production facilities, but a plant was under construction in Nevada and one was being planned in Alaska. Leading producer States in 1963 were California, 13 plants; Pennsylvania, 22 plants; Texas, 16 plants; Michigan, 9 plants; and New York, 12 plants. The 478 million barrels of portland cement production capacity in 1963 was 30 percent in the Eastern United States, 50 percent in the Central States,

and 20 percent in the western part of the country. Capacity was increasing at a relatively more rapid pace in the Central and Western States in line with their relatively more rapid rate of population gain.

In 1963 the U.S. portland cement industry operated at 73.4 percent of capacity. This apparent under utilization of capacity was not as great as it appears due to geographic inequalities, seasonal fluctuations, and obsolete equipment still in use but being operated at high cost and with only a short remaining useful life span.

In general, cement markets have been local, that is, within a radius of 150 to 300 miles from the producing plant. However, with increased use of high-capacity, automated barges and trucks and market center sales and distribution terminals, some producers have expanded their market territories. A company on the Hudson River, for example, has one terminal situated 1,000 miles from its production plant.

An excellent reference map titled: "Portland Cement Plants U.S., Canada, & Mexico" is published biennially by Pit and Quarry Publications, 431 South Dearborn Street, Chicago, Ill. The map shows locations of existing plants and distribution centers and also those under construction. Plant ownership, capacity, and type of production process are also identified for each plant.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Cement, literally, is any substance used to make bodies adhere to each other and includes a great diversity of natural and synthetic materials including asphalt, glue, epoxy resin, lime, plaster, paste, and portland cement. Hydraulic cements are those which have the property of "setting" or hardening under water; nonhydraulic cements do not set under water. This discussion is confined to calcareous hydraulic mineral cements such as portland, portland-slag, natural, masonry, pozzolan, and slag.

Specifications for cements were recommended by the American Society of Civil Engineers in 1885 and accepted by many consumers as standard. Much of the early testing of portland cements was done by government and city engineers using the German standard of 227 pounds per square inch tensile strength after 28 days as a guide. Specifications issued by the American Society for Testing and Materials (ASTM) in 1917 were accepted as U.S. Government standards. Since then, revisions have been made from time to time as various types of cement were produced to meet definite requirements. The latest ASTM cement specifications are too voluminous to include in this report, but the important ones which have been promulgated are listed for each type of cement and may be obtained from the American Society for Testing and Materials.

Clinker is the term used for the pea to golf ball size, partially fused lumps formed in the kiln during cement manufacture by burning a proportioned mixture of raw materials. Chemically, the clinker consists of varying proportions of tricalcium silicate ($3CaO \cdot SiO_2$ abbreviated to C_3S), dicalcium silicate ($2CaO \cdot SiO_2$ or C_2S), tricalcium aluminate ($3CaO \cdot Al_2O_3$ or C_3A), tetracalcium aluminoferrite ($4CaO \cdot A1_2O_3 \cdot Fe_2O_3$ or C_4AF) and minor calcium sulfate ($CaSO_4$), magnesia (MgO) lime (CaO) and various alkalies depending upon the raw materials used, production flowsheet, and type of cement being manufactured.

Portland cement is produced by burning a finely ground mixture containing approximately 75 percent calcium carbonate, 4 percent magnesium carbonate, 14 percent silica, 5 percent alumina, and 1 percent iron oxide at about 2,700° F. The magnesium carbonate is not necessary to the composition but usually occurs mixed with the calcium carbonate in nature. The remaining 1 percent may include impurities such as sulfur, and alkalies. Although limestones and shales or clays are the commonly used raw materials, various combinations of economically available materials are used as may be necessary to make a proper composition. Uniformity of the final product is controlled by careful chemical analysis of the mixture. The clinker kiln product is ground to form the powder sold as portland cement.

Most portland cements approach their ultimate strength in 1 year and reach 65 to 75 percent of their ultimate strength in 7 days; the *high-early-strength type* reaches almost one-half of its ultimate strength in 1 day. In 1940, ASTM grouped portland cements under five types, based partly upon the proportions of tricalcium silicate, dicalcium silicate, and tricalcium aluminate in the cement. Specifications for Type I, general-purpose cement, and Type II moderate-heat cement, are so similar that many companies make only one type that will meet the requirements of either. Type III, high-early-strength cement containing a greater quantity of tricalcium silicate, is made by many companies for use where time cannot be allowed for Type I or II to develop strength. Types I, II, and III together constitute more than 97 percent of all the portland cement in the United States. Type IV, low-heat cement containing less tricalcium silicate and tricalcium aluminate and Type V, high-sulfate resistant cement containing the least amount of trical-

cium aluminate, are usually made only upon order (ASTM Specification C 150–63).

Natural cements, sometimes called Roman cements in Europe, are produced by calcining an impure, argillaceous limestone or dolomitic limestone containing from 15 to 40 percent silica, alumina, and iron oxide at a comparatively low temperature, about 1,400° F, at which decarbonation but no fusion takes place. The burned mass will not slake if water is added, but when ground to a powder it will harden rapidly when mixed with water. Variations in the chemical composition of the limestone bed, used at any particular plant, are reflected in the composition and quality of the finished cement. Natural cements acquire most of their ultimate strength in 5 years and only one-eighth of their ultimate strength in 7 days (ASTM Specification C 10–62 T).

Masonry cements are mixtures of portland or natural cements, finely ground limestone or lime, and a plasticizer additive that are prepared for use as a mortar for laying brick or other masonry work (ASTM Specification C 91–63).

Pozzolan cements are produced by pulverizing mixtures of slaked lime or portland cement clinker with volcanic ash, granulated blast furnace slag, or other pozzolanic material. These *pozzolanic materials*, or *pozzolans* as they are sometimes called, are siliceous or siliceous and aluminous materials, which in themselves possess little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties. These include such natural materials as some of the diatomaceous earths, opaline cherts and shales, tuffs, and volcanic ashes or pumicities; and such artificial materials as precipitated silica and some blast furnace slags and fly ashes (ASTM Specifications C 340–63 T).

Pozzolanic materials also are used as additives to finished portland cement. Some diatomaceous earths have been used in such small quantities as 3 percent of the weight of the cement for improving the workability and preventing segregation of the concrete. In proportions of 10 to 35 percent of the weight of the pozzolan and cement used, the heat of hydration may be less than for some portland cements, and the permeability of concrete in lean mixes may be reduced (*16*).[2]

Slag-lime cements are made by pulverizing mixtures of slaked lime and granulated basic blast-furnace slag. These cements are sometimes considered pozzolan cements even though granulated basic blast-furnace slag contains silicates of calcium and possesses some cementitious value without the addition of slaked lime and therefore is not a true pozzolanic but rather a latent hydraulic material. (ASTM Specification C 358–63 T).

Portland-blast furnace slag cement is sometimes classified as a pozzolanic cement and is made by grinding together portland cement clinker and granulated slag in proportions of about 35 to 50 percent cement and 50 to 65 percent slag (ASTM Specification C 205–63 T).

Air-entraining cement are cements to which an air-entraining agent has been added during grinding. Alternatively, air-entraining agents may be added to a concrete mix instead of being interground with the cement (ASTM Specification C 175–63).

High-alumina cement or aluminous cement is manufactured by burning a mixture of limestone and bauxite containing about 30 percent alumina compared with 5 percent alumina in an ordinary portland cement raw mix. The resultant cement is black in color and has a high-early-strength. The main constituent is monocalcium aluminate ($CaO \cdot Al_2O_3$). There is no American standard specification. The specifications for portland cement are frequently used pending formulation of standards.

Concrete is defined as artificial stone made by mixing cement and sand and gravel, broken stone, or other aggregate. The materials are mixed with sufficient water to cause the cement to set and bind the entire mass (ASTM Specification C 94–63).

A bag of cement is theoretically equal to 1 cubic foot. In the United States for portland cement this is standardized at 94 pounds and for most prepared masonry cement at 70 pounds.

A barrel of cement equals four bags, or 376 pounds of portland cement and 280 pounds of prepared masonry cement.

TECHNOLOGY

Geology and Raw Materials

It requires approximately 3,200 pounds of raw materials (not including fuel requirements) to make 1 ton of portland cement. Depending upon the type of cement being manufactured and the composition of available raw materials, a variety of components are blended to achieve the proper composition of mill feed. For standard Type I portland cement a typical raw blend analysis would be as follows: $CaCO_3$, 75.8 percent; SiO_2, 14.1 percent;

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

$MgCO_3$, 3.5 percent; Al_2O_3, 4.2 percent; Fe_2O_3, 1.6 percent; and alkalies, 0.8 percent.

Theoretically, a large number of mineral raw materials could be blended to achieve the desired raw mix composition, but in practice a comparative few are actually used.

Argillaceous limestone, or "cement rock" as it is often called, close to the desired lime-silica-alumina proportions, is combined with minor quantities of other materials to produce the proper mixture at almost one-fourth of the cement plants.

At others, the necessary lime is supplied by limestone, marl, marble, or oystershell and the alumina and most of the silica and iron oxide by clay, shale, blast-furnace slag, schist, or bauxite. If additional silica is needed, it is obtained by adding quartz sand or sandstone, and additional iron oxide by adding iron ore or iron rich residues.

Sometimes all the raw materials are not available at one place so the supply of the primary raw material, "cement rock" or limestone, usually determines plant location. If suitable clay or shale is closely associated, as is often the case, so much the better.

The major raw materials mentioned are all marine sedimentary in primary origin and an intrinsic property of such rock is relatively uniform chemical and physical character over areas of wide lateral extent. Such materials usually occur flat lying or only moderately inclined from the horizontal plane. These geological factors result in widespread distribution of raw materials usually amenable to large-scale, low-cost open-pit mining (*4, 5*).

Mining

Cement is such a low-priced commodity that every economy of rock-breaking, transportation, grinding, and calcining must be utilized. The rock is recovered from large quarries (or, in some instances, from underground mines), or the marl or shell is dredged from excavations or from offshore deposits.

Large capital investment for cement plants demands that reserves sufficient for many years large-scale operations be proven prior to installation. During mining, every effort is made to design the layout to utilize the largest, most economical machinery. For example, one new plant uses optimum blasting practices to break a week's rock requirements (60,000 tons) with each shot, and employs a 9-cubic yard electric shovel to load 45-ton capacity diesel trucks which haul the broken rock to a 54-inch gyratory primary crusher. The rock is then further reduced in smaller gyratory crushers, hammermills, or other breakers to about ¾-inch size. Later, upon withdrawal from storage piles, the rock is further reduced to less than ¼-inch size in similar tertiary crushing units.

Preparation of Kiln Feed

As the crushed raw materials arrive at the grinding mills, they are automatically weighed and selectively introduced into the plant flowsheet by remotely controlled (in some cases by a computer) proportioning feeders. This system compensates for raw material variables and maintains the uniform feed essential to quality control. The raw grinding unit consists of tube or ball mills in which the mixed raw materials are comminuted to very fine particle sizes, usually 85 percent through 200-mesh or finer.

A few plants use flotation methods to remove objectionable impurities such as excessive silica or silicates from raw materials, enabling more efficient use of quarried materials.

Two different processes that vary in method but not in principle are used in manufacturing cement—the dry process and the wet process. In the former, the material is dried—in most plants during raw grinding—and the mixture is fed into the kilns in a dry state; in the latter, a slurry of controlled consistency is burned. The principal advantages claimed for the wet process are simpler blending of the ground raw materials and elimination of the drying of moist raw materials. It also requires less power than dry grinding. Advantages claimed for the dry process are greater kiln fuel economy and shorter, less expensive kilns. In the United States about 60 percent of installed capacity is wet process and 40 percent dry process.

Kiln Operation

Rotary cement kilns are among the largest pieces of moving machinery used in any industry; kilns up to 600 feet long and 20 feet in diameter are used in the United States (and larger ones are planned). In Japan and the Soviet Union kilns over 600 feet in length are in operation. Cement kilns are steel cylinders lined with the necessary refractories, inclined slightly, and rotated slowly. The fuel, which may be powdered coal, oil, or gas, is blown into the kiln, creating tongues of flame reaching 30 to 50 feet into the kiln. The raw mixture is fed into the upper end of the kiln automatically. Hot gases from the flames in the lower end of the kiln pass over the raw mixture, expelling the moisture and converting carbonates to oxides. As the material descends slowly in the kiln, it reaches the so-called burning zone in the lower one-third of the kiln, where the material reaches the point of incipient fusion, and complex silicates and aluminates are formed. When it emerges from the kiln, it is a new sub-

stance in the form of hard, fine-grained balls called clinker, which is passed through a cooler and sent to large storage sheds.

Cement clinker is relatively inert after it has cooled and may be stored for months without deterioration.

One of the major factors in maintaining a low price for portland cement has been the continuing improvement in kiln design from the original 50-foot length to the present size. Waste heat from the kilns was utilized in many ways in attempts to reduce fuel consumption at the plants. Emphasis in recent years has been placed on better utilization of the heat within the kiln by nodulizing, preheating the kiln feed in the exhaust of the kiln, and preheating the fuel and air with recovered heat from the clinker. Current kiln design favors internal heat exchangers such as a chain zone near the upper end of the kiln by which heat is withdrawn from the kiln exhaust gases by "curtains" of stainless steel chain and transferred to the raw feed as it passes through the hot metal curtain.

When rotary kilns were first used over 2 million Btu were required per barrel of cement produced. Today's average is about 1 million Btu, and a plant at Superior, Ohio, reports 700,000 Btu per barrel using a chain zone.

In recent years, air pollution from plant exhaust stacks became a major factor in many areas, and the dust nuisance of formerly isolated cement plants became part of an expanding problem. More complete combustion has solved part of the problem and elaborate dust collection systems have been incorporated in renovation plans of many plants. Cyclone dust collectors and electrostatic precipitators are now integral parts of most plants, and various ways have been devised to return the recovered dust to the kiln or feed circuit without detrimental effect upon the chemical balance of the mixture.

Control and instrumentation of kilns is also making great strides. Computer control and complete closed loop operation, are in practical use at some plants and being considered or experimented with at many more. Sonic, gamma-ray, and electronic indicators are in general use, and X-ray spectrography providing analyses in a few minutes that used to take 6 or 8 hours permits immediate and accurate plant adjustments for quality control.

Clinker Grinding

When clinker is taken from storage to be ground into cement, approximately 4 to 6 percent of gypsum regulator is added. "Finishing" mills, usually ball mills, grind the clinker to extremely fine particle sizes, over 90 percent through 325-mesh usually expressed in square centimeters of surface per gram of cement. The finished cement is a powder finer than flour or face powder when it leaves the mill.

USES

Portland cement has little utility alone but rather is the material which, in the presence of water, binds minerals aggregate into concrete or as a constituent of mortar will hold building blocks or bricks together.

The addition of water causes a hydrous gel from which various compounds crystallize and interlock giving the hard "set."

The early uses of portland cement concrete in the United States were for foundations, retaining walls, dams, piers, bridge abutments, sidewalks, and for highway and street pavements. All of these were uses where compressive strength and durability were the primary requirements. Many other uses were added when reinforcing steel was imbedded in the concrete to compensate for lack of tensile strength. Buildings of all sorts, residential, commercial, and noncommercial, such as schools and auditoriums, are now built of concrete. The use of lightweight concretes and prestressing techniques has extended the use of concrete to thin-shell roofs with unsupported spans of great lengths and to lightweight bridge decks. Soil cement, made by mixing dry cement with surface soils and subsequently wetting and tightly compacting the mixture, is widely used to pave roads, streets, airports, and parking areas in cases where the strength of a regular pavement is not required.

Excessive expansions of certain concrete structures have been observed, whereas other structures made with concrete containing the same cement but different aggregates have remained in good condition. On the other hand, other concrete structures with poor aggregate, but a different cement, had remained in excellent condition. Some constituents in certain cements react under given conditions with some constituents in certain aggregates. Tests have indicated that the constituent in the cement responsible for the action is the alkali, either Na_2O or K_2O. Laboratory investigations have confirmed the theory that interaction of some of the siliceous constituents of the aggregate with the alkali in the cements causes an alteration of the aggregate material and expansion of the concrete after setting. The substitution of finely pulverized reactive silica or pozzolanic material for part of the cement provided a large area of reactive surface to reduce an initial high alkali concentration. Several other remedial measures, including control of the alkali content of the cement, have been used to avoid undue expansions when alkali-reactive aggregates are

used, but no complete solution has been found.

Increasing variations of cement have come into special use such as white, high-alumina, expansive and oil-well grout cements.

Concrete made with heavy aggregates such as barite or iron ores is in common use at atomic plants where radiation protection is required. Such concrete will shield persons from the gamma and beta irradiation which is the result of the disintegration of radioactive materials. Research also has been conducted on cements of special composition which may have particular utility in radiation shielding (*10*).

New lower cost or improved methods of casting concrete such as prestressing, slip-forming, precasting, and modular construction have made portland cement concrete of increasing interest to builders and architects who are continually creating new free-form and sculptured finish designs, making concrete structures more diverse and attractive in aspect.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

As manufactured by most companies, there are no major byproducts of cement, although prepared masonry cement mixtures are a common coproduct made by mixing finished cement with ground lime or limestone. In preparing a mixture for the kilns, especially when flotation beneficiation is employed, several types of material may be rejected from the kiln mixture. They may be either sent to waste or, if a market can be found, sold as a byproduct of the manufacturing process. Among the materials which have been recovered from the flotation circuit and marketed at times are mica and graphitic fines. Some cement kiln flue dusts have been retained and treated to recover potash. One plant formerly recovered 10 to 15 tons of solid carbon dioxide per day from the flue gas. Various waste rocks necessarily quarried in the selective mining of usable material are crushed and sold as aggregate for concrete.

When demand for cement was weak, some cement plants turned to the manufacture or processing of other materials for which they were equipped and favorably located to handle. These included crushed stone for agricultural use, road stone or flux; fertilizers; and the custom crushing of other minerals or materials. Idle kilns were converted to the production of lime and occasionally to various other uses, such as sintering clays and shales to obtain lightweight aggregates; nodulization or agglomeration of iron ore for open hearth and blast furnaces; production of sponge iron; calcination of petroleum coke, dolomite, and limestone; and drying and calcining bauxite, manganese ore, and phosphate.

ALTERNATE MATERIALS

Cement is an essential constituent of concrete and there is no substitute for cement in this field. As the binder in concrete for engineering construction, such as architectural concrete, highway and airport pavement, residential construction, water and irrigation systems, and many other applications, portland cement has comparatively little competition. However, for many concrete uses the consumer has a choice of alternate materials (such as bituminous concrete for highways) or for using other materials in combination with concrete to lower his concrete requirements. The choice of principal structural material is governed by many factors such as cost, personal preference, and building codes and specifications.

Building tiles, bricks, and blocks can be made of sand and lime by radically improved methods in a steam autoclave, and if costs and physical characteristics are as advantageous as claimed, these materials may become a substitute for portland cement concrete blocks in some applications.

There are many substitute or alternate raw materials for cement manufacture, if they are ever needed. For example, wollastonite could be used as a cement raw material if proportioned properly with other raw materials, and muscovite schist or pretreated spent oil shale can substitute for clay. In Europe some cement is a byproduct of sulfuric acid manufacture from gypsum or anhydrite.

RESERVES

From a world standpoint, there is no problem concerning the abundance and adequacy of raw material and fuel resources for the manufacture of portland cement. There do exist, however, local shortages of suitable raw materials; in some instances it may be cheaper to pay freight charges than to attempt to manufacture the cement locally. Occasionally, local studies will reveal previously unrecognized sources of material that can be utilized with proper blending, mixing, or other treatment.

CONSERVATION PRACTICES IN PRODUCTION AND USES

Industrial waste products may be substituted, in part, for some raw materials. Blast-furnace slag may substitute for clay or shale in the raw mix. Residues from caustic soda production or waste from marble quarries may be used to supply calcium carbonate. Iron oxide may be

obtained from copper smelter residues or wastes from plants obtaining sulfuric acid from pyrite.

As previously mentioned, during burning operations, longer kilns, internal heat exchangers, and preheaters conserve fuel and flue dusts may be recirculated.

Portland-slag cements are made at some plants by grinding granulated blast-furnace slag with portland cement clinker as a means of increasing production without increasing kiln capacity.

Portland cement requirements in concrete is sometimes reduced from 10 to 35 percent by blending fly-ash, slag, spent oil shale, or one of many natural pozzolans such as volcanic tuff or diatomaceous earth with the cement before or during concrete manufacture.

SOURCES OF STATICAL INFORMATION

The Bureau of Mines maintains statistical coverage of cement production and shipments (by both producing district and destination). Raw material and energy requirements, transportation methods, mill values, and plant capacity are surveyed. The Bureau summarizes production statistics from all principal cement producers in the world and compiles U.S. import and export figures from Census Bureau records. Cement data are published monthly in Cement Mineral Industry Surveys and annually in the cement chapter of Minerals Yearbook, volume 1.

The Business and Defense Services Administration of the U.S. Department of Commerce maintains and publishes statistics on costs and consumption of concrete products and ingredients, including cement, in the construction industry.

PRODUCTION, CONSUMPTION AND TRADE

Booms in building result in increased demand for cement; curtailment in civilian construction during wars and business depressions results in rapid loss of market. Even a single program can have substantial impact on the industry. For example, the present huge interstate highway program has used concrete for either paving surface or soil cement or concrete somewhere in the base or sub-base in more than 70 percent of the mileage built through 1963.

World production of cement fluctuated around 300 million barrels per year during the 1920's, 1930's, and first half of the 1940's. From 1946 through 1958 production increased from 500 million to 1.5 billion barrels, and to 2.2 billion barrels in 1963, as more countries developed increased need for cement to enable industrial expansions.

Production of portland cement in the United States increased consistently until 1928 when 176 million barrels of cement was produced. It dropped to 64 million barrels in 1933 before starting to rise again. In 1942 production reached 184 million barrels, but in 1944 had decreased to 94 million barrels. The recovery was more rapid after World War II, and in 1947 production was again 187 million barrels, and has continued to rise consistently, reaching 353 million barrels in 1963.

Finished portland cement is a perishable commodity if exposed to moisture. Stocks of finished portland cement at the producing plants are usually about equal to 1 month's production. Although no figures are available to indicate how much stock is on hand at the customer's level, it is considered to be a very small amount.

As shown in table 1, foreign trade has never assumed much national importance in the U.S. cement industry. Most imported cements have been either used along certain sections of the east coast which are at some distance from the nearest plant in the United States, or they consist of special types which are used in such small quantities that domestic manufacturers find it impractical to manufacture and market them. After World War II, exports were greater than usual because of high demand from underdeveloped nations, but that market for U.S. cements declined owing to the increasing self-sufficiency of those nations and to the increased competition from the revived European cement industry. Manufacturing costs in some countries may be markedly higher than in the United States, but the cost of transporting U.S. cements makes locally produced cement cheaper on a delivered basis.

Imports from other countries into the United States are subject to duties as follows: Roman (natural), portland and other hydraulic cements and cement clinker (except from Communist countries, in which case the rate is 6 cents per 100 pounds), 2¼ cents per 100 pounds; white nonstaining cement, 3 cents per 100 pounds (8 cents for Communist countries).

TABLE 1.—*Summary of statistics of the cement industry* [1]

	1954–58 (average)	1959	1960	1961	1962	1963
United States: [2]						
Production:						
Portland—thousand barrels	299,228	339,091	319,009	324,114	336,488	352,543
Prepared masonry—do	[3] 15,372	16,205	14,553	14,289	15,004	15,506
Natural, slag, and hydraulic lime—do	[3] 805	438	568	225	440	357
Total—do	315,405	355,734	334,130	338,628	351,932	368,406
Capacity used at portland-cement mills—percent	85.7	80.7	73.7	73.2	71.8	73.8
Shipments from mills:						
Portland—thousand barrels	294,616	335,452	312,292	320,751	331,823	349,253
Prepared masonry—do	15,314	16,174	14,247	14,354	14,892	15,636
Natural, slag, and hydraulic lime—do	795	441	548	269	402	352
Total—do	310,725	352,067	327,087	335,374	347,117	365,241
Value of shipments [4]—thousands	$950,303	$1,161,849	$1,103,680	$1,122,483	$1,149,405	$1,178,980
Average value per barrel	$3.06	$3.30	$3.37	$3.35	$3.31	$3.23
Stocks at mills, Dec. 31—thousand barrels	23,243	31,530	35,725	36,619	39,229	39,597
Imports—do	3,589	5,265	4,108	3,621	5,633	4,030
Exports—do	1,521	277	187	286	380	460
Apparent consumption—do	312,793	357,055	331,008	338,709	352,370	368,811
World: Production—do	1,356,056	1,726,233	1,855,952	1,954,987	2,098,128	2,201,159

[1] Barrel as used in this report, unless otherwise stated, refers to a 376-pound barrel.
[2] Includes Puerto Rico.
[3] Portland cement, 1954–58; and masonry and natural 1955–58.
[4] Value received f.o.b. mill, excluding cost of containers.

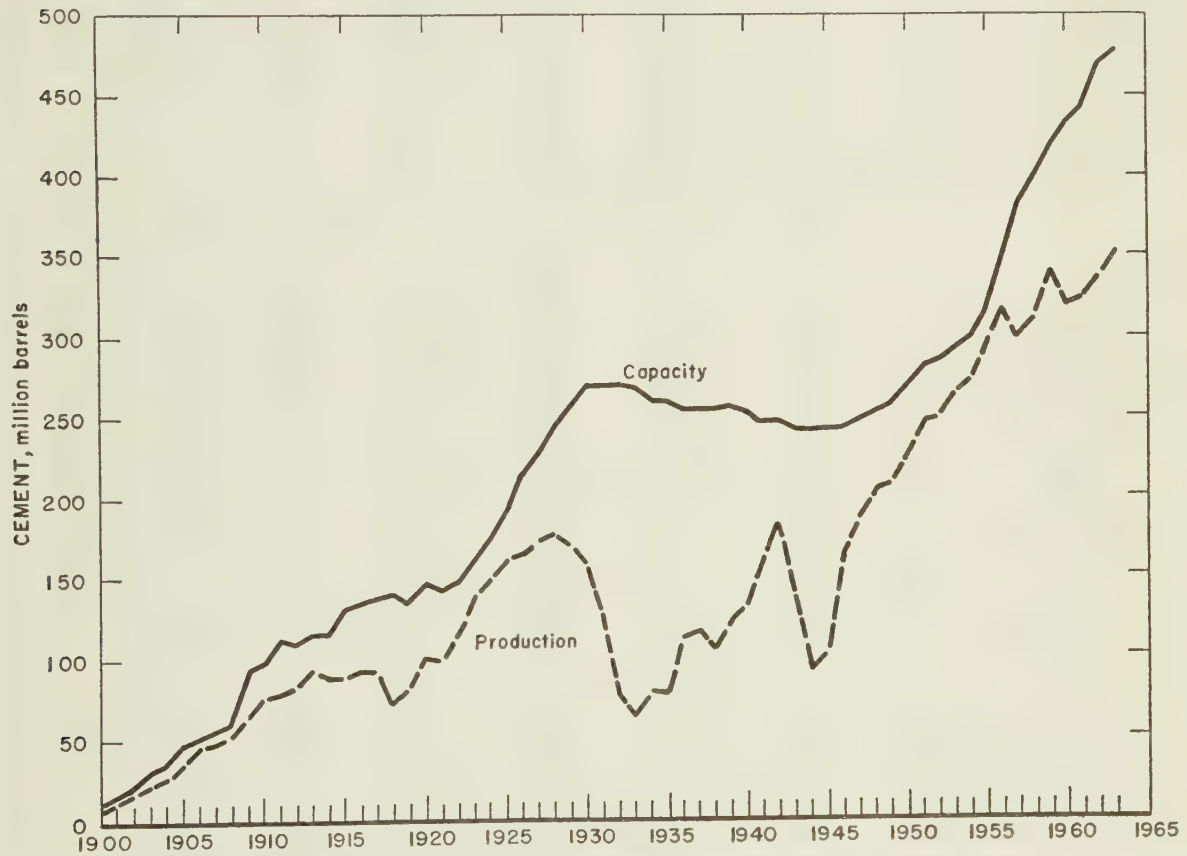

FIGURE 1.—Annual Production and Capacity of Portland Cement in the United States.

TABLE 2.—*World production of hydraulic cement by countries* [1]

[Thousand barrels]

Country	1954–58 (average)	1959	1960	1961	1962	1963
North America:						
Canada (sold or used by producers)	27,188	33,427	30,782	33,010	36,587	37,314
Cuba	3,301	3,670	[2] 2,345	[2] 1,760	[2] 1,760	[2] 2,050
Dominican Republic	1,395	1,114	998	1,390	1,507	1,343
El Salvador	405	487	504	440	381	457
Guatemala	516	680	657	733	680	921
Haiti	[3] 199	223	281	258	299	270
Honduras	----------	64	199	246	328	352
Jamaica	774	1,155	1,243	1,266	1,173	1,179
Mexico	13,175	15,884	18,112	17,795	19,654	21,577
Nicaragua	211	205	188	229	270	317
Panama	428	569	639	668	633	[2] 633
Trinidad	668	1,055	1,038	575	973	909
United States (including Puerto Rico)	312,870	355,734	334,130	338,628	351,932	368,406
Total	361,130	414,267	391,116	396,998	416,177	435,728
South America:						
Argentina	12,284	13,884	15,485	17,021	17,127	14,629
Bolivia	182	170	223	264	293	340
Brazil	18,446	22,521	26,232	27,610	29,739	30,395
Chile	4,462	4,902	4,855	5,101	6,725	6,837
Colombia	6,667	7,968	8,590	9,334	10,237	10,759
Ecuador	833	921	1,179	1,284	1,137	1,419
Paraguay	59	76	82	94	100	111
Peru	3,201	3,412	3,518	3,483	4,110	4,421
Uruguay	2,052	2,474	2,433	2,281	2,193	1,994
Venezuela	8,572	10,976	8,719	8,871	9,000	9,205
Total	56,758	67,304	71,316	75,343	80,661	80,110
Europe:						
Albania	317	434	428	704	[2] 704	[2] 880
Austria	11,351	14,172	16,593	18,082	17,924	19,372
Belgium	26,373	26,027	25,728	27,874	28,073	27,610
Bulgaria	5,000	8,402	9,300	10,255	11,100	12,929
Czechoslovakia	19,214	27,558	29,616	31,328	34,300	33,421
Denmark	6,919	8,150	8,455	9,287	9,569	[2] 8,854
Finland	5,758	6,860	7,370	7,904	7,956	8,320
France	67,815	82,080	83,101	90,183	98,984	104,367
Germany:						
East	18,628	24,655	29,504	30,958	31,873	32,014
West	108,360	135,817	146,025	159,153	167,649	171,308
Greece	6,801	8,467	9,598	10,771	[2] 10,876	[2] 13,022
Hungary	6,344	8,402	9,211	9,393	10,161	10,542
Iceland	41	457	428	440	569	575
Ireland	3,541	3,682	4,368	4,362	4,456	4,702
Italy	65,118	84,443	93,895	105,721	118,274	129,509
Luxembourg	1,003	1,126	1,231	1,354	[2] 1,350	[2] 1,350
Netherlands	7,054	9,381	10,542	11,158	11,815	12,202
Norway	5,295	6,631	6,749	7,470	8,279	8,261
Poland	24,397	31,175	38,651	43,177	44,233	44,972
Portugal	5,383	6,045	7,024	7,294	8,214	8,402
Rumania	12,289	16,716	17,907	19,396	20,457	25,617
Spain (includes Canary Islands)	27,153	33,591	33,614	38,862	42,767	41,893
Sweden	14,623	16,535	16,452	17,660	17,907	19,056
Switzerland	12,911	15,731	17,801	21,114	21,847	20,996
U.S.S.R.	150,728	227,402	266,897	299,028	335,967	357,661
United Kingdom	72,535	74,992	79,137	84,291	83,587	82,086
Yugoslavia	9,938	13,017	14,060	13,691	14,764	16,570
Total	694,889	891,948	983,685	1,080,910	1,163,655	1,216,491

See footnotes at end of table.

TABLE 2.—*World production of hydraulic cement by countries* [1]—Continued

[Thousand barrels]

Country	1954–58 (average)	1959	1960	1961	1962	1963
Asia:						
Afghanistan [4]		199	217	240	[2] 410	557
Burma	270	211	264	235	311	727
Ceylon	440	557	498	481	498	440
China	37,150	71,943	79,150	46,900	46,900	52,770
Cyprus	[5] 369	487	516	557	575	563
Hong Kong	698	833	879	1,079	1,243	1,272
India	30,389	40,668	45,939	48,337	50,342	54,851
Indonesia	1,161	2,017	2,269	2,609	2,996	[2] 2,996
Iran [4]	1,343	3,395	4,673	4,368	[2] 4,368	[2] 4,368
Iraq	2,674	3,876	3,624	5,494	5,400	5,283
Israel	3,835	4,579	4,726	4,960	5,594	5,992
Japan	75,549	101,247	132,147	144,448	168,787	175,594
Jordan	528	645	967	1,308	1,378	1,671
Korea:						
North	3,876	11,293	13,398	13,263	13,931	14,834
Republic of	645	2,099	2,527	3,067	4,632	4,562
Lebanon	2,738	4,356	5,007	5,125	5,048	5,254
Malaya	616	1,132	1,677	1,941	1,917	2,123
Pakistan	5,095	5,875	6,796	7,288	8,179	8,783
Philippines	2,697	4,263	4,661	5,975	5,635	5,576
Saudi Arabia		[2] 440	[2] 528	616	891	[2] 891
Syrian Arab Republic	1,806	2,621	2,867	3,166	3,559	4,016
Taiwan	3,911	6,256	6,936	8,824	10,970	13,128
Thailand	2,375	2,990	3,084	4,673	5,646	5,840
Turkey	6,186	10,167	11,949	11,891	13,597	15,737
Viet-Nam, North [2]	1,196	2,234	2,392	2,685	2,709	2,932
Total	185,547	284,383	337,691	329,530	365,516	390,760
Africa:						
Algeria	4,151	5,611	6,227	6,285	3,811	5,183
Angola	580	909	944	921	991	1,137
Cameroon, Republic of	[3] 59	[2] 64				
Cape Verde Islands	[6] 18	53	23	41	[2] 40	[2] 40
Congo (Leopoldville)	2,422	2,035	[2] 1,175	821	[2] 950	[2] 910
Ethiopia	170	147	164	176	240	199
Kenya	950	1,841	2,070	1,935	2,029	1,994
Morocco	3,442	2,943	3,401	3,694	4,093	4,368
Mozambique	862	1,249	1,302	1,243	1,050	[2] 1,114
Nigeria		721	985	2,134	2,492	3,137
Northern Rhodesia	3,453	797	[2] 745	715	[2] 704	[2] 704
Southern Rhodesia		2,486	[2] 2,597	1,636	[2] 1,466	[2] 1,466
Nyasaland		205	[2] 176	217	[2] 176	[2] 176
Senegal	780	1,003	985	1,067	1,073	1,114
South Africa, Republic of	14,336	15,520	15,860	15,233	15,591	16,910
Sudan	[3] 410	586	709	487	498	[2] 586
Tunisia	2,076	2,592	2,375	2,105	2,128	2,117
Uganda	405	481	422	369	328	322
United Arab Republic (Egypt)	8,250	10,460	12,002	12,553	13,562	14,072
Total	42,364	49,703	52,162	51,632	51,222	55,549
Oceania:						
Australia	12,688	15,333	16,364	16,757	17,197	18,288
New Zealand	2,680	3,295	3,618	3,817	3,700	4,233
Total	15,368	18,628	19,982	20,574	20,897	22,521
World total (estimate) [1]	1,356,056	1,726,233	1,855,952	1,954,987	2,098,128	2,201,159

[1] This table incorporates some revisions.
[2] Estimate.
[3] Average annual production 1955–58.
[4] Year ended Mar. 20 of year following that stated.
[5] Average annual production 1956–58.
[6] Average annual production 1957–58.

TABLE 3.—*Portland cement shipments from mills in the United States,[1] by types*

Type and year	Active plants	Shipments		
		Thousand barrels	Value	
			Total (thousands)	Average per barrel
General use and moderate heat (types I and II):				
1954–58 (average)	161	274,492	$820,227	$2.99
1959	171	312,970	1,012,836	3.24
1960	175	290,968	962,453	3.31
1961	174	298,616	980,371	3.28
1962	177	309,784	1,004,793	3.24
1963	180	326,918	1,032,809	3.16
High-early-strength (type III):				
1954–58 (average)	108	11,516	40,071	3.48
1959	129	14,363	53,484	3.72
1960	135	13,772	51,731	3.76
1961	135	14,305	53,000	3.71
1962	141	14,597	53,576	3.67
1963	145	14,559	51,167	3.51
Low-heat (type IV):				
1954–58 (average)	1	13	51	3.92
1959	3	10	46	4.44
1960	3	8	32	4.07
1961	2	14	60	4.23
1962	2	9	37	4.45
1963	3			
Sulfate-resisting (type V):				
1954–58 (average)	7	135	505	3.74
1959	11	192	743	3.86
1960	14	435	1,664	3.83
1961	13	416	1,608	3.87
1962	11	244	1,048	4.29
1963	18	324	1,267	3.91
Oil-well:				
1954–58 (average)	16	1,552	5,215	3.36
1959	16	1,182	4,121	3.49
1960	14	1,059	3,669	3.46
1961	14	1,235	4,181	3.39
1962	13	1,215	4,140	3.41
1963	15	1,158	3,878	3.35
White:				
1954–58 (average)	4	1,150	6,923	6.02
1959	4	1,515	9,819	6.48
1960	4	1,384	9,274	6.70
1961	5	1,532	10,387	6.78
1962	5	1,668	11,690	7.01
1963	5	1,935	13,547	7.00
Portland-slag and portland pozzolan:				
1954–58 (average)	10	4,598	14,220	3.09
1959	8	3,806	12,864	3.38
1960	7	3,525	12,057	3.42
1961	8	3,316	11,179	3.37
1962	7	2,868	9,524	3.32
1963	8	2,620	8,681	3.31
Miscellaneous: [2]				
1954–58 (average)	23	1,160	4,202	3.62
1959	22	1,414	5,331	3.77
1960	20	1,141	4,366	3.83
1961	19	1,317	4,992	3.79
1962	19	1,438	5,581	3.88
1963	23	1,739	6,625	3.81
Grand total:				
1954–58 (average)	161	294,616	891,414	3.03
1959	[3] 172	335,452	1,099,244	3.28
1960	[3] 176	312,292	1,045,246	3.35
1961	[3] 175	320,751	1,065,778	3.32
1962	[3] 178	331,823	1,090,389	3.29
1963	[3] 181	349,253	1,117,974	3.20

[1] Includes Puerto Rico.
[2] Includes hydroplastic, plastic, and water proofed cements.
[3] Includes number of plants making air-entrained portland cement as follows: 1959, 119; 1960, 120; 1961, 120; 1962, 121; and 1963, 121.

TABLE 4.—*Prepared masonry cement shipments from mills in the United States*

Year	Active plants	Shipments		
		Thousand 280-pound barrels	Value (thousands)	Average value per barrel
1954–58 (average)	121	14,817	$53,801	$3.63
1959	134	16,174	61,155	3.78
1960	140	19,134	56,485	2.95
1961	143	19,275	55,737	2.89
1962	144	19,998	57,405	2.87
1963	143	20,997	59,599	2.84

TABLE 5.—*Natural, slag, and hydraulic-lime cement shipments from mills in the United States*

Year	Active plants	Shipments		Average value per barrel
		Thousand 376-pound barrels	Value (thousands)	
1955–58 (average)	5	795	$2,567	$3.23
1959	4	441	1,450	3.29
1960	4	548	1,949	3.56
1961	4	269	968	3.60
1962	4	402	1,611	4.01
1963	4	352	1,407	4.00

GOVERNMENT PROGRAMS

Although little direct action was taken by the Government regarding cement production during World War II, orders by the War Production Board stopping all nonessential public and private construction effectively curtailed cement production in most of the country.

The defense program of World War II, particularly in Texas and California, gave impetus to demand for cement in those States and in certain other areas throughout the United States. Construction of Army and Navy installations, large atomic plants, airfields, and the like required large quantities of cement and caused such dislocations in nearby cement trade channels as local shortages and rationing, and temporary unavailability of cement.

The Area Redevelopment Administration and the Farmers Home Administration, as part of their programs include local cement production facilities in their consideration of means to implement their areal improvement objectives.

The Federal Trade Commission monitors acquisitions and mergers within the industry to prevent lessening of competition or creation of monopolies within market areas or industry segments.

Under the regulations of the Anti-Dumping Act, the Treasury Department audits cement imports to insure that they are not sold below a reasonable price. The U.S. Army Corps of Engineers, Bureau of Reclamation, Geological Survey, Bureau of Standards, and Bureau of Mines all maintain programs on particular areas

of cognizance concerning quality testing of cement, and concrete, or inventory of raw materials.

PRICES AND COSTS

Cement price patterns are so complex that no simple portrayal is possible. Discounts for cash and large quantity, freight absorbtions, and bagging costs vary with the local markets. Local prices for 20 United States and 2 Canadian cities with current discounts and special charges are published monthly in Engineering News-Record. The Bureau of Mines publishes quarterly, only the f.o.b. mill value of cement in bulk.

When the American portland cement industry began in the late 19th century, cement was $3 per barrel, and after 80 years of price fluctuation to a low of 81 cents per barrel in 1909, the price was approximately $3.35 in 1960. Since 1960, overcapacity and concomitant competition has forced average value down to $3.20 in 1963.

The percentage increases in price for cement have lagged far behind competing building materials such as lumber. Since 1930, other building materials have increased five times in price but cement prices have increased only three times.

Cement prices reflect reduced costs due to operation of larger and more efficient equipment and greater output per man-hour. In addition, capital investment for new plants has declined from about $30 per barrel of installed annual capacity in 1946 to from $6 to $12 per barrel. This lower unit investment is due primarily to the trend toward larger capacity plants and production machinery.

However, the increasing use of local distribution terminals to hold or expand markets under present rigorous competition has partly offset savings in production plant investment. These distribution terminals cost $200,000 to $2 million each to build.

Labor costs have been reduced by use of higher capacity machinery combined with centralized controls with electronic or automatic equipment. One operator can now supervise production steps which formerly may have required several dozen production workers. X-ray spectrography has reduced personnel requirements in the analytical laboratory. The amount of labor required to manufacture a barrel of cement is estimated to range from 6 to 15 man-minutes depending upon size and degree of automation of the plant. If employment costs are estimated at $3.50 per hour then there is from 36 to 88 cents labor in producing a barrel of cement. In 1963, an estimated 26,000 persons were employed in cement plants and the quarries or mines serving them.

TAXES

Most of the ordinary cement raw materials are granted a percentage depletion of 5 percent. A few, for example fuller's earth, quartzite, metallurgical and chemical limestone, and diatomaceous earth, are granted the 15 percent rate.

TRANSPORTATION AND PACKING

Transportation cost restrains the volume of imports and exports, limits the market area of the individual plant, and plays a major role in governing the movement of cement within an area and from one area to another. The general effect of the so-called Basing Point Decision (*12*), which declared illegal any practice whereby cement companies would agree to quote certain prices for their products at designated pricing points, forbids collusive pricing but allows absorption of freight charges by individual firms acting independently to permit them to compete in the available market.

Specially designed equipment is used to handle cement in bulk. Originally, shipments of cement were in barrels to protect the product from exposure to moisture, but the barrel has not been used as a container for many years. In 1963, over 85 percent of the shipments of cement was in bulk and nearly all the rest in paper bags.

However, the traditional units of measure, 94-pound bags (1 cubic foot of portland cement) with four bags equal to one 376-pound barrel is still used in the United States. An exception is prepared masonry cement which is measured in 280-pound barrels.

Bulk transportation is by special automated trucks, railroad cars, ships, and barges which are self-unloading and eliminate costs of packing and containers. Cement firms operate 200 distribution centers including storage silos for bulk cement to service local markets and some large users, such as ready-mixed concrete companies, have similar storage facilities.

For the small proportion of cement still packaged, pneumatic handling, automatic baggers and palletizers, and spring conveyors have increased efficiency. Improved plastic-lined bags have reduced to a minimum losses due to sack breakage and moisture absorbtion.

RESEARCH

The Portland Cement Association, Chicago, Ill., conducts technical research, provides an information service, undertakes promotional and educational efforts (including safety work), and develops new or improved products and methods. The broad program of the Association is financed out of dues contributed by the majority of the cement manufacturers of the United States and all cement manufacturers in Canada.

Through the publication and application of its own research findings, its cooperation with other research and technical organizations, and the daily contact of its own engineering staff with the problems of the designer and builder, the Association functions as a clearing house for information on portland cement, the making of concrete, concrete design procedures and construction methods.

In 1950 the Association completed the first section of its new research and development laboratories at Skokie, Ill. Additional facilities were opened in 1958. These laboratories are the largest and most completely equipped laboratories in the world devoted exclusively to research and development in the uses of portland cement and concrete. In addition, field laboratories and experimental projects are maintained at other locations. The Association conducts many experimental programs including work on items such as shrinkage control, air-entrained concrete, the water-cement ratios of concretes, soil-cement, pressure grouting, tilt-up construction practices, prestressing methods and materials, precasting, and cement hydration.

Many individual companies maintain small experimental laboratories and a few have fairly large research establishments. One firm has been testing the Pyzel vertical fluidized reactor system for producing low-alkali cement.

Many private, commercial, and engineering college laboratories conduct tests and experiments, usually on the various phases of concrete manufacture and use rather than on cement as such.

The American Concrete Institute gathers, correlates, and disseminates information for the improvement of the design, construction, manufacture, use, and maintenance of concrete products and structures. Through its Technical Activities Committee and Standard Committee standard specifications, practice recommendations, and definitions are developed and promulgated.

The Bureau of Standards conducted an important international symposium on cement chemistry in 1960 (*8*). The Bureau of Reclamation tests cement and concrete mixtures for use in dam construction. The Bureau of Mines conducts studies on the use of concrete in mining supports, bulkheads, linings, and ground stabilization or sealing by grouting techniques, and also tests natural pozzolan raw materials.

OUTLOOK

The cement industry will continue to expand both in response to population growth and to growing need in highway and industrial and housing construction.

Cement requirements in 1975 may be estimated by projections based on several pro-syllogisms. These are actual past cement production, population growth, gross national product, and value of construction. Cement production (in million barrels) in 1975 by each method would be 500, and 646 respectively. These figures assume population will increase a 1.6 percent compounded annually, gross national product in constant dollars at 3.8 percent per year and construction value (constant dollars) at 4.8 percent annually during the projection period. Respective average annual increases since World War II (to 1963) have been 1.7, 3.6, and 4.8 percent. It is therefore estimated that cement production in 1975 will be more than 500 million barrels. Some cement experts feel that the high projection, 646 million barrels based on construction value in constant dollars is the most valid criterion, but cement production increases since World War II do not substantiate this estimate.

The continued development of new methods of using cement and concrete and improvements and new variations in the product constantly offer new opportunity for America's builders and new challenges for the imagination and ingenuity of our architects and engineers. Prestressed concrete, soil-cement paving, thin-shell cantilevered concrete roofs, sculptured and exposed aggregate panels, lightweight concrete, expansive cement, precasting, slip-form casting and factory-built modular units are all recent stimulants.

The high initial investment required in the industry hinders the formation of new firms. Present ownership patterns will continue, for the most part, and these established firms will develop most of the new capacity in the industry. As new capacity is completed, some older, obsolescent high-cost production plants will be deactivated.

Advances in technology such as increased thermal efficiency (or even new type kilns), more complete automation, and large, low unit-cost production machinery will continue to hold production costs in check and assist in maintaining or improving cement's competitive posture against other traditional building materials. The introduction of new synthetic panels is not expected to have much effect on cement requirements, but they will compete instead with lightweight non-load-bearing materials such as wallboard, plaster, wood, plywood, glass, thin-gauge metal, and stone veneers.

Reserves of raw materials, including fuels required for cement production, are adequate for many years. Particular quarries now providing material to some plants may be exhausted, but other sources are expected to replace them without undue hardship. In addition, many alternate raw materials that have never been used for cement manufacture in the United States, exist in quantity if ever needed.

PROBLEMS

The cement industry's major current problem is improving its cost-price ratio in the face of fierce intra-industry competition. This is important to permit development of new capital for investment in replacing obsolete, and installing new, production capacity that will be needed to supply projected cement needs of the country.

The apparent close approach to practical limits on the size of rotary kilns presents a challenge to develop new type kilns or other production equipment with increased efficiency and concomitantly lower costs.

The complete solution to the problem of weakness of concrete in tension still presents a challenge to research engineers, although prestressed concrete has made a giant step in this direction.

Statistics on cement market areas and on use patterns are not collected or disseminated in sufficiently refined detail to completely satisfy the needs of market analysts in this sensitive, high-volume market place. Finished cement is perishable and must be stored in enclosed silos of definite capacity so that production and shipments are closely tied to local short-term market projections.

The continued development of stable, serviceable concrete that will not develop either shrinkage cracks or require expansion joints remains a challenge.

Obsolete building codes, in some localities, preclude optimum use of new concrete types, products, and methods. Coordination of structure design and quality of construction workmanship is difficult. This causes wasteful overdesign as a defensive measure. Vertical integration of the industry permitting broader quality control over concrete manufacture and construction workmanship has been proposed as a means of overcoming this problem.

Even though more than 85 percent of the cement shipped is in bulk the majority of the American industry continues to use the antiquated system of barrels and bags in its accounting procedures instead of tons and pounds or the metric weight system. The fact that various countries use different weights for their standard bag and barrel makes world statistics difficult to correlate. Even in the United States, a bag or barrel of masonry cement does not equal the same measure of portland cement. The use of bags and barrels in the existing technical literature causes many persons to oppose a change in the weight system.

In some locations the production of a low alkali cement compatible with reactive aggregates remains a technical problem.

Dust is still considered a nuisance problem by neighbors of a few plants.

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CESIUM

By Donald E. Eilertsen [1]

CESIUM, a metal highly reactive with air or water, was discovered in 1860 and came into small commercial use in 1926. The major commercial sources of cesium have been pollucite and a residue derived from processing lepidolite to lithium hydroxide. Currently imported pollucite from pegmatites is the commercial source of cesium; not much is known about cesium resources. Various methods have been developed to extract cesium from pollucite; the acid leaching process is commonly used.

Cesium has applications such as in photomultiplier tubes, infrared lamps, scintillation counters, and spectrophotometers. One of cesium's major problems is the lack of large-scale uses. Moderate increases in the consumption of cesium and its compounds are predicted for conventional applications. However, larger consumption of cesium could result if uses as a rocket propellant and in generation of electrical energy develop.

BACKGROUND

Cesium was discovered in 1860 and isolated in 1881, while pollucite was discovered in 1846 but was not postively identified until 1864. Cesium had practically no industrial use until 1926, but thereafter for a few years it was used to coat filaments in tungsten vacuum tubes. Pollucite was first mined in the United States in Oxford County, Maine, from 1926 to 1929. Prior to 1957, very small domestic supplies of cesium raw materials were available. In 1958, the American Potash & Chemical Corp. began recovering cesium compounds from residues of a Texas plant that extracted lithium hydroxide from imported lepidolite. The residue, known as ALKARB, was the major commercial source of cesium for a short time. Currently, imported pollucite is used as the commercial source of cesium.

SIZE AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

In recent years, six firms in the United States have extracted cesium commercially. They are American Potash & Chemical Corp., Trona, Calif.; Dow Chemical Co., Midland, Mich.; Penn Rare Metals (subsidiary of Kawecki Chemical Co.), Revere, Pa.; MSA Research Corp., Callery, Pa.; Rocky Mountain Research, Inc., Denver, Colo.; and U.S. Industrial Chemicals Co., Cincinnati, Ohio.

[1] Commodity specialist.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Cesium (Cs) is soft, silver white, and the eighth lightest metallic element (*2*)[2]. It is the heaviest of the alkali metals, explodes violently when brought into contact with water, and ignites spontaneously, burning with a brilliant blue flame, when contacted with air (*5*). Some of its other properties are atomic number, 55; atomic weight, 132.91; density, 1.87 g/cm^3 at 20° C; melting point, 28.5° C; boiling point, 705° C; ionic radius, 169 A; and ionization potential, 3.87 volts.

Typical analyses of cesium metal and compounds follow (*5*):

Elements	Cesium metal, percent		Cesium compounds, percent
Cesium, minimum	99.5	99.9	99.9
Sodium, maximum	.11	.01	.01
Potassium, maximum	.01	.01	.005
Rubidium, maximum	.10	.01	.05
Lithium	[1]	[1]	[1]
Calcium, maximum	.10	.01	----------
Silica, maximum	.01	[2].005	----------
Iron and aluminum, maximum	.01	.001	.001
Calcium and barium, maximum	----------	----------	.01

[1] Not detected.
[2] Average.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

ALKARB.—A dry product formerly made in San Antonio, Tex., from end liquor resulting from the extraction of lithium values from lepidolite. It consisted of mixed alkali carbonates usually containing about 2 percent cesium and 20 to 25 percent rubidium carbonates. Lithium operations in the United States no longer use lepidolite as a source of lithium.

TECHNOLOGY

Mineralogy, Geology, and Mining

Cesium and rubidium often occur together in nature. The earth's crust is estimated to contain 7 parts per million of cesium compared with 310 parts per million of rubidium.

Pollucite, a mineral resembling quartz, is well known for its high cesium content. The chemical formula of pollucite is essentially $H_2O \cdot 2Cs_2O \cdot 2Al_2O_3 \cdot 9SiO_2$, and on this basis it contains 40.1 percent cesium or 42.5 percent cesium oxide (Cs_2O). Lepidolite, carnallite, and beryl occasionally contain cesium. Field tests for cesium have been developed to help prospectors identify the element (*1*).

Cesium occurs in certain granites and granite pegmatites; granites have been estimated to contain an average of 60 parts per million of cesium.

Pollucite and lepidolite are recovered commercially from pegmatites. They are mined as a coproduct with other valuable pegmatite minerals, usually by open-pit techniques ranging from large mechanized operations to small ones employing mostly hand labor. Rich ore shoots have been extracted by underground methods. Hand-sorting methods are generally used to recover pollucite.

Metallurgy

Recovery From Pollucite

Cesium can be extracted from its mineral concentrate by various methods such as acid leaching, basic fusion followed by water leaching, and direct reduction of the mineral concentrate. The acid leaching process is commonly used, and any one of a number of acids may be utilized to prepare the concentrate for the recovery of cesium.

One method used to extract cesium from pollucite is briefly described as follows (*4*):

Ground pollucite concentrate is treated with hydrobromic acid and then filtered to remove silica. The soluble bromides of cesium, other alkali metals, and aluminum are treated by a modified solvent extraction process utilizing isopropyl alcohol to remove aluminum bromide. The cesium and other alkali metal bromides are then evaporated, water is removed, and the mixed alkali bromides are treated in an extractor, where liquid bromine is added. After this reaction, the mixture is filtered to remove the alkali metal bromides. The resultant cesium tribromide solution is evaporated. Bromine is liberated, and the high-purity cesium bromide formed is reduced with a reactive metal to high-purity cesium metal.

Recovery From Lepidolite Residues

Two extraction methods to recover cesium salts from lepidolite residues are described as follows (*3*):

The first step in the chlorostannate method involves dispersing carbon dioxide flue gas in the starting solution of mixed alkali carbonates to precipitate 70 percent of the contained potassium as potassium bicarbonate. The remaining alkali carbonates are converted to chlorides. The cesium is then precipitated by adding only enough stannic chloride initially to form insoluble cesium chlorostannate. The more soluble rubidium remains in solution and subsequently is precipitated by adding excess stannic chloride. The cesium chlorostannate precipitate is purified by dissolving it with hydrochloric acid, reducing it to the stannous state, and then reprecipitating pure cesium chlorostannate. Cesium chlorostannate may be decomposed to the chloride by pyrolysis, electrolysis, or reduction with iron.

The alternate ferrocyanide method is used if the ferrocyanide or carbonate forms are the desired cesium end products. Sodium zinc ferrocyanide is added to the mixed alkali carbonate solution to precipitate cesium zinc ferrocyanide. The cesium zinc ferrocyanide can be decomposed to mixed carbonate by heating in air. A water leach dissolves only the cesium carbonate from the roasted material, and the resulting cesium carbonate solution is evaporated to dryness.

Reduction of Compounds to Metal

Cesium metal has been prepared in many ways. One method is to reduce cesium carbonate by reacting it at red heat with a metal. This process yields high-purity cesium, oxides of the reductant utilized, and carbon. Alternate promising reduction methods include heating cesium hydroxide with aluminum or magnesium in a stream of hydrogen, reacting cesium chloride vapor with heated calcium carbide (or calcium metal) under vacuum, and vacuum reduction of cesium fluoride with magnesium. Cesium metal has been produced experimentally by electrolysis, but this method has not proved economically feasible to date.

Because cesium is highly reactive, the metal must be recovered under an inert oil in a suitable receiver.

USES

In recent years quantities of cesium have been consumed in research and development of ionic propellent engines and generation of thermoelectric power, both of which have attracted widespread attention particularly for spaceflight applications.

In the ion engine, vaporized cesium is diffused through a heated porous plate. The cesium atoms become positively charged ions, and an electric field accelerates the positive ions to a velocity of approximately 300,000 miles per hour. The high-velocity ions are exhausted through a nozzle to develop thrust.

Thermionic converters under development convert heat to electricity by the thermionic activity of cesium plasma. One thermionic generator using five cesium diodes and solar energy was reported capable of generating 100 watts of electrical power.

In addition to these large potential applications, moderate quantities of cesium are used in the manufacture of photomultiplier tubes, infrared lamps, scintillation counters, and spectrophotometers.

Cesium is the active agent in producing electricity from light.

During World War II, cesium was used in infrared lamps for invisible signaling; in sniperscopes and snooperscopes similar to devices now in use by some night watchmen, guards, and border patrols; and in the photocell in the nose of the "homing" projectiles to track, intercept, and destroy enemy planes in flight.

An atomic clock which has an accuracy of 5 seconds in 300 years is operated with cesium.

Cesium iodide and cesium bromide crystals are used in some scintillation counters because they emit electrons when exposed to nuclear radiation. Cesium bromide infrared spectrophotometers are available to measure semiconductor epitaxial film thickness.

Certain cesium salts have been used in the medical field as an antishock after administering arsenical drugs.

Cesium may be used as a scavenger of gases and other impurities in chemical processing and in both ferrous and nonferrous metallurgy. It is used as an absorbent to remove impurities at carbon dioxide purification plants and acts as a catalyst in various hydrogenation and polymerization processes.

Besides being used as a source of cesium and rubidium, ALKARB is used in glass, ceramic glazes, and porcelain enamels where the alkalies modify the chemical and physical properties of the product.

BYPRODUCTS AND ALTERNATE MATERIALS

Pollucite is usually mined as a byproduct of lepidolite or beryl, and its production is dependent upon profitable sale of those minerals. ALKARB was recovered as a byproduct of processing lepidolite for lithium. The quantities of cesium- and rubidium-bearing carbonates and liquors available depend upon lepidolite consumption for lithium production. Cesium is rarely used as a substitute for other alkali metals because of its relatively high price.

Germanium, tellurium, selenium, and their compounds are alternate infrared-sensitive materials. Rubidium, potassium, thorium, mercury, and uranium tetrafluoride are possible substitute ion fuels.

RESERVES

Information on the resources of cesium is meager, and that which is known has been developed mostly as a result of prospecting, exploring, and producing other minerals from pegmatites, particularly lithium minerals. The principal commercial source of cesium is pollucite.

Some pollucite was produced from mines in Oxford County, Maine, and from the Tin Mountain mine near Custer, S. Dak., during the 1920's. A resource of pollucite may still exist in these deposits.

The largest known deposits of pollucite are those in the lithium-bearing pegmatites at Bernic Lake, Manitoba, Canada, which tentatively have been estimated to contain 350,000 tons of pollucite containing 20 percent cesium and substantial rubidium.

Rough estimates indicate that deposits in the Bikita district of Southern Rhodesia contain 150,000 tons of pollucite while deposits in the Karibib area of South-West Africa contain 50,000 tons of pollucite.

Cesium occurs in a number of other minerals such as lepidolite and in brines and saline deposits, but information on these cesium resources is scant.

SOURCES OF STATISTICAL INFORMATION

The Bureau of Mines canvasses the domestic cesium industry annually for statistical data on cesium source materials and cesium metal and compounds. Much of this data is withheld from

publication to avoid disclosing company confidential statistics.

PRODUCTION, CONSUMPTION, AND TRADE

In 1962, 50 tons of pollucite was reported mined in South Dakota. The cesium industry imports its supplies of pollucite for consumption mostly from Southern Rhodesia. Some pollucite has come from Mozambique and Canada.

Considerably more pollucite was consumed to produce cesium metal and compounds in 1963 than in 1962, but the overall consumption of pollucite continued to be small. Cesium metal production in 1962 was reported at 159 pounds. Statistical data on cesium and its compounds for 1963 are withheld to avoid disclosing company confidential information.

Import data on cesium compounds have been available since September 1963. Preliminary figures for 1964 showed imports of 106 pounds of cesium chloride valued at $5,802, and 1,915 pounds of other cesium compounds valued at $59,821, all from United Kingdom and West Germany. No data on exports of cesium metal and compounds were available.

Pollucite is imported duty free. Cesium metal is dutiable at 17 percent ad valorem, while cesium chloride and other cesium compounds are dutiable at 12.5 and 10.5 percent, respectively.

STRATEGIC CONSIDERATIONS

The cesium industry in the United States is dependent on imports for its supply of pollucite.

No lepidolite is being processed to lithium in the United States at present; consequently, there is no ALKARB production.

Cesium is not on the list of materials for stockpiling in the national strategic and supplemental stockpiles.

PRICES

Prices quoted for 99+ percent cesium during 1963 and 1964 were $100 to $375 per pound.

TAXES

The domestic and foreign depletion allowances for cesium are each 15 percent.

TRANSPORTATION AND SAFETY MEASURES (*5*)

Major precautions should be taken in handling, transporting, and storing cesium metal, because cesium is very reactive with water and air. Cesium is available packed under argon or in vacuum in Pyrex glass vials or returnable stainless steel cylinders. The vials of cesium are wrapped in aluminum foil and packed with vermiculite (expanded mica) in metal cans for protection against shock and fire. Cylinders of cesium are hermetically sealed and firmly supported in wood boxes filled with vermiculite.

Cesium compounds are not as dangerous as the metal. Nevertheless, they should be handled carefully and transported in closed containers for protection against contamination, deterioration, attack on the skin and membranes by some salts, and possible fire hazards.

RESEARCH

Cesium has been studied intensely by the Government in recent years in connection with the development of the ion engine. Testing of the engine in orbital flight is planned for 1965.

Cesium also has been studied intensely for thermoelectrical power.

The Bureau of Mines research on cesium and rubidium in recent years has been concerned with the development of concentration methods for pollucite, extraction and separation of cesium and rubidium, purification of cesium and rubidium salts, and determination of some of the thermodynamic properties of certain cesium compounds.

OUTLOOK

Moderate increases in consumption of cesium and its compounds are predicted for conventional applications. Large consumption of cesium could result if uses as a rocket propellant and in generation of electrical energy develop.

A few new pollucite deposits will probably be discovered and worked in the next 5 to 10 years as a result of the growing interest in cesium, but the major supply of cesium in the United States will continue to come from hand-sorted pollucite from Southern Rhodesia, South-West Africa, and Canada. Use of pollucite flotation concentrate will come closer to reality.

Occasional price cuts of cesium metal and compounds may occur as a result of increased demand for these products and perhaps as a result of improving methods to produce these materials.

PROBLEMS

Numerous problems confront cesium, extending from discovery of deposits through extraction, refinement, and the development of uses.

Cesium occurrences are numerous, especially in pegmatites, brines, and saline deposits, but information is lacking on the nature and extent of cesium in specific deposits.

Hand-sorted pollucite is currently the commercial source of cesium. Some success has been achieved experimentally in upgrading pollucite from ores rich in pollucite, but a problem exists in developing methods to conentrate pollucite economically from low-grade ores.

Costly multistage techniques employed to extract cesium from hand-sorted pollucite are largely responsible for the high prices of cesium metal and compounds. Methods to extract cesium simply and cheaply from this material as well as from various grades of pollucite flotation concentrate, other minerals, brines, and saline deposits are needed.

The lack of information on the physical and chemical properties of cesium hinders the progress of applied research and the development of uses. Furthermore, the alloying characteristics of cesium, particularly the development of intermetallic compounds, have not been extensively investigated.

Special precautions must be taken in preparing, handling, packaging, storing, and transporting cesium metal as the element is extremely reactive. Cesium ignites spontaneously in air, and reacts explosively with water; mists containing cesium compounds are caustic. Consequently steps taken to handle cesium safely contribute to the high prices of cesium products.

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CHROMIUM

By R. W. Holliday [1]

CHROMIUM, best known as decorative plating, is indispensable in a broad range of other industrial applications. It is the chief alloying constituent of stainless steel. Chromium compounds are important chemical materials, and the mineral, chromite, is a major refractory.

The United States imports virtually all of its chromite, the only commercial chromium mineral. Domestic production was small even from 1951 to 1961, when the Government purchased chromite at incentive prices for stockpiling.

In the last decade the metallurgical industry accounted for about 60 percent of the total domestic chromite consumption, the refractory industry consumed 28 percent, and the chemical industry 12 percent.

Turkey, Southern Rhodesia, and Republic of South Africa have been major sources of metallurgical ore imports to the United States. The U.S.S.R. resumed shipment of chromite to the United States in 1959, after several years' suspension, and has become an important source. In the past most refractory ores came from Cuba and the Philippines. However, the Philippines and the Republic of South Africa are now principal suppliers. The Republic of South Africa is by far the largest source of ores used by the chemical industry.

Stainless steel accounts for about 65 percent of the consumption by the metallurgical industry and other alloy steel for about 25 percent.

Chromite refractory products are used principally in furnace linings. Being chemically neutral, they are especially useful in areas such as the slag line of basic open-hearth furnaces to separate the basic magnesite brick bottoms from the acid silica brick sides.

Chromium chemicals are used as pigments, in surface treatment and corrosion control of metals, in leather tanning, and in numerous other applications. The principal chromite chemicals are derived from sodium bichromate.

World consumption of chromite is expected to increase as world industrialization progresses. Southern Africa eventually will become the source for most of the world supply of chromite as high-grade reserves in other areas become depleted.

Problems include the need for lower cost mining and concentrating procedures plus wider consumer acceptance of fines and concentrates. Improved ductility and impact resistance of the metal and its alloys are needed. Other problems relate to discovery and exploration of deposits, transportation, and the need for better statistical data on foreign resources and consumption.

BACKGROUND

First discovered in Siberia as a lead chromate about 1765 and isolated as a metal in 1797, chromium was used primarily in the manufacture of chemicals until the early years of this century. Chromite deposits were discovered in Maryland and Pennsylvania about 1827 and these were the major world source until the discovery of Turkish ores in 1848. Although production was small by present standards, the U.S. deposits provided a basis for establishing a domestic chromium chemicals industry which has become the world's largest. Unsuccessful attempts to manufacture chrome yellow in 1828 and 1833 were followed in 1845 by a successful plant which produced potassium bichromate for American textile mills and pigment manufacturers. This early product led to development of a broad range of new chromium chemicals and new uses. After 1900 chromium gained importance as a constituent of alloys and as a refractory.

Ferrochromium has been known since 1820

[1] Commodity specialist.

through the studies of Faraday and Stodarts, and also by the work of Berthier. About 1860, Baur found that ferrochromium was the best material for adding chromium to steel. Other experimental work was done by Fremy, Percy, and Mushet. In 1873, Bierman, of Hanover, announced that his firm was producing ferrochromium commercially. By 1886 there were several regular producers of ferrochromium. Production of ferrochromium in the electric furnace began in 1899, replacing the blast furnace for this use. According to Brennan (*2*),[2] in 1906, the Electro Metallurgical Co. (Union Carbide) began producing ferroalloys at Niagara Falls as an extension of its predecessor companies in Virginia and West Virginia. Frederick Mark Becket joined the Niagara Falls organization in its beginnings and his early work resulted in the silicon reduction methods employing silicon or silicides for the production of low-carbon alloys, particularly low-carbon ferrochromium. Variants of Becket's methods are still used for the bulk of the low-carbon ferrochromium produced today.

World production of chromite increased from an estimated 59,000 short tons in 1900 to 4 to 5 million tons per year in 1954–63. Although a deposit in Harford County, Md., was the major world source from about 1827 until discovery of Turkish ores in 1848, most subsequent production has come from the Eastern Hemisphere.

From about 1930 till the end of World War II, Cuba was the principal U.S. source of refractory chromite. Since then Philippine (Masinloc) ore has been the standard refractory chromite, although in the last decade a new type from the Transvaal in the Republic of South Africa has won acceptance by the refractories industry. This African ore is higher in chromium and iron, and lower in alumina and silica, than the Cuban and Philippine ores. Reserves are virtually unlimited.

Most of the chromite consumed by the metallurgical industry is first converted in the electric furnace to one of several chromium ferroalloys. Stainless steel containing 12 percent or more chromium comprises the largest single use in the United States. Some chromite is converted to chromium metal for addition to special alloys, and some chromite in the mineral form is added directly to steel.

Processing by the refractory industry essentially involves sizing, blending, and necessary forming and curing or firing. Most of the chromite used by the chemical industry is converted first to sodium dichromate by roasting (with soda ash), leaching, and chemical separation.

[2] Italicized numbers in parentheses refer to numbers in the list of references at the end of this chapter.

SIZE AND ORGANIZATION OF THE INDUSTRY

Some chromite was mined in the United States in every year between 1899 and 1962; none was mined in 1962 or 1963. The domestic industry can supply only an insignificant part of domestic requirements. Total imports to the United States in 1954–63 averaged about 1.6 million short tons annually.

Some domestic consumers mine and import chromite through foreign affiliates or subsidiaries. Others purchase chromite through U.S. importing firms. Major foreign producers and U.S. importers were listed in a 1962 publication (*3*).

Eight domestic companies, operating 14 plants, produced 300,000 tons of chromium ferroalloys in 1963. Two firms produced chromium metal. These products were consumed for the most part by the steel industry, but about 5 percent went into high-temperature and other alloys.

Eight companies, operating 14 plants, consumed 358,000 tons of chromite in the manufacure of refractory products. Four companies operating six plants produced 130,000 tons of chromium chemicals, sodium bichromate equivalent.

GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

The domestic chromite mining industry, inactive in 1962 and 1963, is in California, Montana, Oregon, and Alaska. Distribution of the domestic consuming industry is given in table 1.

Foreign chromite production is virtually all in the Eastern Hemisphere. Based on 1963 data major producers, in descending order, are the U.S.S.R., the Republic of South Africa, the Philippines, Turkey, Southern Rhodesia, Albania, Iran, and Yugoslavia.

A tabulation of ferrochromium producers (*12*) listed world productive capacity in 1961 at slightly more than 1 million tons of high- and low-carbon ferrochromium, and this was expected to increase to 1.25 million tons by 1965. Of the total, North and South America were credited with 43 percent; Europe, excluding the Communist nations, with 32 percent; the Far East with 11 percent; and Czechoslovakia, East Germany, the U.S.S.R., and Yugoslavia with 14 percent. A significant increase was listed for Africa by 1965 (from about 20,000 to more than 100,000 tons).

TABLE 1.—*Principal U.S. consumers of chromite and producers of chromium products*

Company	Plant	Products
METALLURGICAL		
Baltimore Works of the Armco Steel Corp. (formerly Rustless Iron & Steel Co.).	Baltimore, Md	Stainless steel and iron.
Chromium Mining and Smelting Corp [1]	Riverdale, Ill	Exothermic high- and low-carbon ferrochromium; exothermic silicon-chromium alloy.
Union Carbide Corp., Metals Division	Niagara Falls, N.Y. Alloy, W. Va. Marietta, Ohio	Low- and high-carbon ferrochromium briquets; chromium metal; ferrochromium-silicon alloys; exothermic ferrochromium; exothermic silicon-chromium alloy.
Interlake Iron Corp	Beverly, Ohio	High- and low-carbon ferrochromium; ferrochromium-silicon.
Montana Ferro-Alloys Co., Inc., a subsidiary of Chromium Mining and Smelting Corp.	Woodstock, Tenn	High-carbon ferrochromium; ferrochromium-silicon.
Ohio Ferro-Alloys Corp	Brilliant, Ohio	Low- and high-carbon ferrochromium; ferrochromium-silicon; low- and high-carbon exothermic ferrochromium; exothermic ferrochromium-silicon.
Pittsburgh Metallurgical Co	Calvert City, Ky. Charleston, S.C. Niagara Falls, N.Y.	High-carbon ferrochromium; ferrochromium-silicon.
Shieldalloy Corp., Division of Metallurg, Inc.[1]	Newfield, N.J.	Chromium metal.
Tennessee Products & Chemical Corp.	Chattanooga and Rockwood, Tenn.	High- and low-carbon ferrochromium; chromium briquets; ferrochromium-silicon.
Vanadium Corp. of America	Niagara Falls, N.Y. Graham, W. Va. Vancoram, Ohio	Low- and high-carbon ferrochromium; chromium briquets; ferrochromium-silicon; chromium-bearing foundry alloys.
REFRACTORIES		
Basic Refractories, Inc.	Maple Grove, Ohio	Refractory shapes and mortars.
Eastern Stainless Steel	Baltimore, Md.	
General Refractories Co.	Baltimore, Md. Gary, Ind. Los Angeles, Calif.	
Harbison-Walker Refractories Co.	Baltimore, Md. Hammond, Ind. Warm Springs, Calif.	
Kaiser Aluminum & Chemical Corp.	Columbiana, Ohio Moss Landing, Calif.	
E. J. Lavino & Co.	Plymouth Meeting, Pa. Newark, Calif.	
Howe Sound Co., Refractories Division [2]	Conshohocken, Pa.	
Ohio Fire Brick Co.	Oak Hill, Ohio	
CHEMICAL		
Diamond Alkali Co.	Painesville, Ohio Kearny, N.J.	Principally sodium bichromate.
Imperial Color and Chemical Department of Hercules Powder Co.	Glens Falls, N.Y.	
Solvay Process Division, Allied Chemical Corp. (formerly Mutual Chemical Co. of America).	Baltimore, Md.	
Pittsburgh Plate Glass Co.	Jersey City, N.J.[3] Corpus Christi, Tex.	

[1] Does not use chromite.
[2] Processes raw chromite for use by refractories manufacturers, steel companies, and miscellaneous.
[3] Jersey City, N.J., plant was discontinued in October 1963.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Chromite is the only commercial chromium mineral. Basically it is comprised of the oxides of chromium, iron, aluminum, and magnesium in varying quantities, all in solid solution. Traditionally, consumers in the United States have tended to classify the high-chromium chromite as metallurgical grade, the high-iron chromite as chemical grade, and the high-aluminum chromite as refractory grade. However, the different types are used interchangeably to some extent and the lines of distinction are not clearly defined. The national stockpile ore-purchase specifications, table 2, provide a reference that approximates commercial usage.

In practice, limited quantities of fines are used by both the metallurgical and the refractory industries. Acceptance of chromite as a refractory is based primarily on physical properties determined by performance tests, rather than on chemical composition.

In the past, most refractory ore has come from the Philippines and Cuba, but a type of chromite from South Africa has gained acceptance by the refractories industry. It approximates chemical-grade chromite in composition but is lower in silica, and tests have shown that it possesses the necessary refractory characteristics.

Ferrochromium is an alloy of chromium and iron used chiefly as a carrier for addition of chromium to iron or steel. Major classifications are based on carbon and silicon content as shown in table 3.

High-carbon ferrochromium is used to make medium and high-carbon steels of relatively low chromium content. Low-carbon ferrochromium is used in producing stainless, corrosion, and heat-resisting steels of low-carbon and high-chromium content. Foundry ferrochromiums are high in silicon. The low-chromium ferrochomium is known as charge grade because it is used in the initial charge in making stainless and other steels. Other chromium ferroalloys contain higher carbon or silicon, and some contain oxidizing agents, such as sodium nitrate, to react exothermically when added to molten iron or steel. Table 3 lists typical compositions.

TECHNOLOGY

Geology (*3*)

Chromite is used as a general name for all chromium-bearing spinels except the pure end members magnesiochromite ($MgCr_2O_4$) and ferrochromite ($FeCr_2O_4$) and is often expressed as (Mg, Fe) (Cr, Al, Fe)$_2O_4$. Chromite ranges in color from dark brown to black; it is usually opaque, but sometimes translucent. The streak is dark brown. Its luster is submetallic and its hardness 5.5 on Mohs' scale. The specific gravity ranges from 4.0 to 4.6 and the melting point from 1,545° C to 1,730° C. The fracture is uneven and the ore is brittle to tough.

Chromite occurs in peridotites and their derivative serpentines (pyroxenites and amphibolites) and in certain basic and ultrabasic stratified igneous rock complexes. The chromite deposits in peridotite and serpentine occur erratically as irregular or lenticular masses ranging in size from a few pounds upward to a million tons or more. The largest deposits occurring in stratified igneous complexes are uniform over large areas, and some exposures can be traced for tens of miles. Chromite also

TABLE 2.—*National stockpile ore-purchase specifications*

[Weight-percent, dry base]

Grade	Cr:Fe ratio, minimum	Cr_2O_3, minimum	Fe maximum	Cr_2O_3+Al_2O_3, minimum	SiO_2, maximum	S maximum	P maximum	CaO maximum	MgO
Metallurgical [1]	3:1	48.0			8.0	0.08	0.04		
Refractory [2]		31.0	12.0	58.0	6.0			1.0	([3])
Chemical [4]		44.0			5.0				

[1] Specification P-11-R1, June 4, 1956. This specification covers chromite ore suitable for use in the production of commercial ferrochromium and special chromium alloys. All chromite ore shall be lumpy and shall be hard, dense, nonfriable material of which not more than 25 percent shall pass a 1-inch sieve (ASTM Designation E 11). Chromite ore of a friable nature, regardless of an initially lumpy appearance, shall be rejected.

[2] Specification P-12-R3, Dec. 4, 1963. This specification covers refractory-grade chromite which is satisfactory for production of standard refractory brick. All refractory-grade chromite shall be hard, dense, nonfriable lump ore. Not more than 15 percent by weight of each lot shall pass a U.S. Standard Sieve No. 16 (ASTM designation E 11). Chromite ore of a friable nature, regardless of an initially lumpy appearance, shall be rejected. In addition to complying with the chemical and physical requirements of this specification, the chromite ore shall be from sources and of a type that is used, directly without chemical modification or processing, by at least 3-manufacturers of standard refractory chrome brick in the United States that consume at least 50 percent of the refractory chromite.

[3] Not specified but to be determined for each lot and reported.

[4] Specification P-65-R, Jan. 5, 1961. This specification covers chromite ore satisfactory for use in the manufacture of chromium chemicals. All chromite ore shall be of a friable nature.

TABLE 3.—*Composition of typical commercial grades of ferrochromium and chromium metal*

[In percentages of principal constituents][1]

Grade	Chromium	Silicon	Carbon	Sulfur	Other
Ferrochromium:					
High-carbon ferrochromium:					
Regular grade	66–70	1– 2	4–6		
Charge grade	50–56	4– 7	6–8	[2]0.03	
Charge grade	58–63	3– 6	5–8	[2].03	
Blocking and foundry grade	55–63	8–12	4–6	[2].03	
Silicomanganese grade	60–65	4– 6	4–6		Manganese 4–6.
Medium-carbon ferrochromium	60–65	[2] 3	2. 5–3		
Low-carbon ferrochromium:					
Regular grade	65–73	[2] 1. 00	0.025–2		
Vacuum grade 1	63–66	5– 7	.010–.025		
Vacuum grade 2	68–71	[2] 2. 00	.010–.025		
Nitrogen grade	67–71	0. 03– 1	.1		Nitrogen 0.75–6.
Ferrosilicon-chromium	50–54	28–32	[2]1.25		
Ferrochromium-silicon:					
34/46 grade	33–36	45–48	[2].05		
40/43 grade	39–41	42–45	[2].05		
55/24 grade	52–57	23–27	[2].05		
57/15 grade	55–59	13–17	[2].05		
60/10 grade	58–62	8–12	[2].05		
65/5 grade	63–67	3– 7	[2].05		
Chromium metal:					
High-carbon chromium metal	87–90		9–11		Iron 0.40.[2]
Low-carbon chromium metal	[3] 97	[2] 1	[2].1–5		Iron 1.20.[2]
Electrolytic chromium metal	[3] 99. 8				Iron 0.20.[2]

[1] Difference between sum of percentages shown and 100 percent is chiefly iron content.
[2] Maximum.
[3] Minimum.
Source: Reference (*5*).

occurs in detrital deposits formed by the weathering of peridotite and serpentine.

Mining

Chromite ores are mined by conventional methods adapted to the peculiarities of individual deposits. Opencut mining varies with the thickness of overburden, the size of deposit, and the mechanical equipment available. Underground methods are dictated by such factors as width and depth of the vein, characteristics of the wall rock, and available equipment. Narrow, high-grade veins may be extracted by resue methods. Flat-lying beds involve scraping for underground transport of the broken rock. Timbering, pillars, cribbing, or backfill may be used for ground support. Access may be through winze, adit, or shaft. With growing acceptance of fines and concentrates by consumers, a continuing trend to less selective mining methods can be expected.

Ore Beneficiation

The traditional use of lumpy ores for metallurgical and refractory applications largely eliminated any beneficiation, other than hand sorting and screening, until recent years. However, improvements in metallurgical practice are bringing greater acceptance of fines and concentrates by consumers, and depletion of ore deposits in some areas has prompted efforts to improve recovery.

Most concentration of chromite involves gravity methods such as jigs, tables, or spirals. Jigs are limited to larger particle sizes, and tables, though probably most efficient, are more costly than spirals. Grinding is necessary to liberate the chromite from gangue minerals, and this generates slimes which usually are rejected because of the cost of further treatment. Chromite ores can also be concentrated by flotation, by use of magnetic or electrostatic devices, and by use of a heavy medium.

Upgrading by physical methods is limited by the chromic oxide (Cr_2O_3) content of the chromite mineral; iron and other molecular constituents of the mineral can be removed only by chemical or pyrometallurgical procedures.

Processing

Chromium can be added directly to iron or steel as ore, but usually it is added as one of the chromium ferroalloys. Chromium metal is used to form alloys with metals other than iron or steel and in some special alloys (*3*, *16*, *19*).

High-carbon ferrochromium is produced by carbon reduction of chromite, usually in a three-phase submerged-arc electric furnace. Carbon and silicon content of the alloy are controlled by the use of flux, by blending of ores, and by changes of the operating temperature.

Medium-carbon ferrochromium is produced from high-carbon ferrochromium, usually by refining in an open-arc furnace with chromite or by blowing with oxygen in a Bessemer converter. Chromite, lime, silicon, and fluorspar are added to the molten high-carbon ferrochromium in the first of these methods. This is the preferred method in the United States.

Low-carbon ferrochromium is made by a two-stage silicon-reduction process. There are three principal variations, known as the basic process, the duplex process, and the ore fusion process.

In the basic process, ferrochromium silicon, produced as a first stage, is crushed, mixed with ore, lime, and fluorspar, and refined in an open-arc furnace to reduce the silicon. (The ferrochromium silicon is made either by direct smelting of ore, quartz, and coke or by smelting high-carbon ferrochromium with quartz and coke.)

The duplex process is similar but involves the use of an oxidizing agent such as sodium nitrate to induce an exothermic reaction. In the ore fusion process, a molten mixture of ore and lime is reacted with ferrochromium silicon and refined.

A number of special chromium ferroalloys are produced by modified charge and melting procedures. These include exothermic, high-silicon, and nitrogen or manganese-containing alloys.

Chromium metal is produced commercially in the United States by two methods. Three-fourths of the domestic output is obtained by electrolysis from a chromium-alum solution deriving its chromium from high-carbon ferrochromium. This process, developed by the Bureau of Mines (*13*), was first used commercially in 1954. Various other electrolytes also have been used, including chromic acid which is used for producing decorative chrome plating. An aluminothermic process is the second commercial method currently used in the United States. An exothermic reaction between chromic oxide and metallic aluminum powder in refractory-lined containers yields chromium metal of a quality that can be controlled by use of purified raw materials and variations in the production method. Other reductants such as silicon, carbon, calcium, sodium, and hydrogen also have been used. Ultrapure, ductile chromium has been produced experimentally by various methods. A Bureau of Mines method involves hydrogen treatment of high-purity electrolytic chromium (*1*, *4–5*, *7*).

Chromite refractories utilize raw ore alone or in combination with other materials, principally magnesia. They are marketed as bricks or shapes either fired or chemically bonded, as moistened or dry aggregates which can be poured or rammed into place, and as mortars and cements. Processing consists essentially of blending, crushing and grinding, screening and proportioning of grain sizes, mixing and tempering, molding, drying, and in some instances firing (*19*). Although refractory-grade ore traditionally has come from Cuba and the Philippines, a more recent development has been the use of ore from South Africa, utilizing sufficient high-purity magnesia to counteract the adverse affects of silica and iron oxides.

Most chromium chemicals are derived from sodium bichromate. Although various ores have been used in its production, the domestic chemical industry has largely standardized on Transvaal grade B friable chromite. This ore contains about 44 percent Cr_2O_3 and is low in silica which is considered the most objectionable impurity because it increases the consumption of alkali and lowers the fusion temperature, causing difficulties in roasting.

Manufacture of sodium bichromate involves roasting a mixture of finely ground chromite, soda ash, and lime; cooling, water leaching, and filtering; evaporation to a concentration of 40 to 45 percent sodium chromate (Na_2CrO_4); and treatment, usually with sulfuric acid, to convert the sodium chromate to sodium bichromate ($Na_2Cr_2O_7$). Concentration then is accomplished by evaporation (*6*, *18*).

USES

In the last decade (1954–63) the metallurgical industry accounted for 59.8 percent of total domestic chromite consumption (gross weight), the refractory industry accounted for 28.4 percent, and the chemical industry consumed 11.8 percent.

As noted earlier, most chromite consumed by the metallurgical industry is converted to ferroalloys and then consumed in the manufacture of stainless, high-speed, and other alloy steels. The consumption, by end uses, of ferroalloys and metal in 1963 is shown in table 4.

In quantities up to about 0.5 percent, chromium refines the grain and reduces segregation in alloy steels. From about 0.5 percent to 1.5 percent, chromium increases hardenability, inhibits graphitization at elevated temperatures,

and increases toughness. In quantities from 2 to 6 percent, chromium imparts high hardness and some corrosion resistance (*3*).

Outstanding resistance to corrosion and oxidation is imparted by additions of 12 percent or more chromium and it therefore is an essential constituent of stainless steels. More than half of the domestic stainless production is of the chromium-nickel and chromium-nickel-manganese (austenitic) type with chromium content ranging between 16 and 26 percent. Chromium appears in a wide variety of other alloy steels ranging in chromium content from less than 1 percent to as high as 35 percent.

In cast iron, chromium improves heat and wear resistance.

Many of the "superalloys" combine chromium with one or more metals, especially iron, nickel, cobalt, molybdenum, tungsten, or columbium. They find use in aircraft and space applications, atomic energy applications, and in the chemical, food processing, oil-refining, and steel industries.

Nickel-base chromium alloys embody resistance to heat and corrosion. They are used in thermocouples, jet engines and turbine blades, furnace equipment, heating elements, and handling equipment for hot or corrosive chemicals.

Cobalt-base chromium alloys are used where there is a need for hardness and corrosion resistance, oxidation resistance, and strength at elevated temperatures. They are used as metal-cutting tools, hard-facing materials, permanent magnets, and gas turbine blades.

Small quantities of chromium are also used in aluminum, copper, and titanium-base alloys.

Chromium metal is used in alloys where impurities are objectionable. It is also used in powder metallurgy and in the production of chromium carbide, used in some hard-facing and abrasion-resistant applications.

Chromite refractories are used in metallurgical and glassmaking furnaces and in limekilns. Because of their chemically neutral character, a major use is at the slag line of basic open-hearth furnaces to separate the basic magnesite brick bottom from the acid silica brick side.

The largest consumption of chromium chemicals is in the manufacture of pigments, and in leather tanning, textile processing and electroplating; but many other uses are important (*18*). Chromium chemicals are essential in the graphic arts. They are employed in fungicides and in a wide variety of chemical processes as catalysts, oxidants, etc.

Chrome plating is done from an electrolyte consisting of an aqueous solution of chromic acid. Chromate film coatings, anodizing of aluminum, and surface diffusion or chromizing are also important methods for protecting metals against corrosion.

TABLE 4.—*Consumption of chromium ferroalloys and chromium metal in the United States in 1963, by major end uses*

[Short tons, gross weight]

	Low-carbon ferro-chromium	High-carbon ferro-chromium	Ferro-chromium silicon	Exothermic ferro-chromium silicon	Chromium briquets	Other [1]	Total
Stainless steels	96,529	55,047	60,754	3	527	93	212,953
High-speed steels	564	1,012	39	----------	----------	17	1,632
Other tool steels	749	1,764	58	----------	----------	25	2,596
Other alloy steels [2]	14,341	38,903	6,921	4,120	390	11,070	75,745
Gray and malleable iron	366	4,305	510	1	304	502	5,988
High-temperature alloys	5,955	701	226	----------	23	1,128	8,033
Nickel-base alloys	321	30	----------	----------	----------	65	416
Other nonferrous alloys [3]	426	1,372	----------	----------	16	695	2,509
Total (gross weight)	119,251	103,134	68,508	4,124	1,260	13,595	309,872
Chromium content	82,151	66,178	28,870	1,695	700	7,221	186,815

[1] Includes exothermic high-and low-carbon ferrochromium, chromium metal, and other chromium alloys.

[2] Includes quantities believed used in producing high-speed and other tool steels and stainless steels because some firms failed to specify individual uses.

[3] Includes cutting and wear-resistant alloys, hard-facing alloys, welding rods, electrical-resistance alloys, and other nonferrous alloys.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Large potential chromium resources exist in laterite deposits in Cuba, the Philippines and elsewhere. However, no commercial process has been developed for extracting the chromium. The Nicaro plant in Oriente Province, Cuba, was designed to extract only nickel from these ores, rejecting iron, chromium, and some cobalt.

ALTERNATE MATERIALS

Alloys, plastics, and various composite materials offer a wide range of possible substitutes for chromium-bearing alloys. To some extent alumium trim can be used in place of chrome-plated trim. Chromizing or other surface treatment permits the use of chromium-surfaced steel as a substitute for more expensive stainless steel. A large-scale research effort over the last 10 to 15 years has been directed toward development of oxidation-resistant coatings for molybdenum, tungsten, and other high-melting-point metals. This research will undoubtedly influence the future use of chromium-bearing superalloys.

Magnesite can be substituted for part of the chromite used in the manufacture of some refractory products.

SECONDARY SOURCES AND RECOVERY

Stainless-steel scrap is the major source of secondary chromium. In 1963, the domestic gross weight consumption of stainless-steel scrap by the steel industry was 719,000 short tons, compared with stainless-steel production of 1 million tons. Other alloy steels and chromium-bearing special alloys also provide secondary chromium. These materials usually are remelted with no attempt to separate chromium from the other alloy constituents. However, at least one firm in the United States is recovering chromium (and other elements) in the form of salts. Certain of the superalloys reportedly are shipped to West Germany for recovery of constituent elements. Slags produced during the melting of various steels contain up to about 12 percent chromium that is not recovered.

RESERVES AND RESOURCES

World reserves and potential resources are estimated to total 2,660 million long tons, distributed as shown in table 5. World production in 1963 was less than 5 million tons. However, a great preponderance of the world resource is in only two nations; 2,000 million tons are in the Republic of South Africa and 600 million tons are in Southern Rhodesia. A second consideration is that about 84 percent of the total is high-iron, 16 percent high-chromium, and only 0.06 percent high-aluminum material.

U.S. chromite ores that are commercial by present standards are insignificant in relation to U.S. requirements. More than 90 percent of the domestic chromite resource is in low-grade, high-iron deposits, with by far the largest occurrence in the Stillwater complex, a layered igneous mass exposed over 30 miles in Stillwater and Sweetgrass Counties, Mont. The overall resource in this deposit is estimated at about 14 million long tons of ore ranging from 15 to 30 percent Cr_2O_3. Physical concentration of the Stillwater ore is limited because the iron is chemically combined as part of the chromite mineral. Operations at one property, during 1943, produced a concentrate averaging 38.8 percent Cr_2O_3 with a chromium-iron ratio of 1.44:1.

Other low-grade deposits of significant size are in the John Day district in Grant County, Oreg., in beach sands along the Oregon coast, and in Eldorado County, Calif. Small scattered deposits of higher grade chromite are known in several other counties of California, in Oregon, and in Alaska. Occurrences also are known in Idaho, Maryland, North Carolina, Pennsylvania, Texas, Washington, and Wyoming. Locations of chromite deposits in the United States and descriptions of domestic and foreign deposits have been published (*3*, *17*).

The largest chromite resource in Canada is in eastern Manitoba, in the Bird River igneous complex, which is similar to the Stillwater complex of Montana. The reserve is conservatively estimated at 9 million tons (to a depth of 660 feet) over a length of 6 miles. The chromite is even higher in iron than the Stillwater and yields lower grade concentrates.

Three chromite-producing areas in eastern Cuba have reserves totaling some 1.25 to 1.5 million tons of shipping-grade ore. The Mayari district yields metallurgical ore. The Camagüey and Moa-Baracoa districts produce refractory ore. A large potential also exists in Cuban laterites and serpentines, which are estimated to comprise some 3,000 million tons of material containing 1 to 4 percent chromium. However, no commercial extractive procedure has yet been developed. Chromite resources of Brazil have been estimated at a few hundred thousand tons, principally of milling-grade ores. Limited production has come from scattered deposits in Guatemala, but the known reserve is small.

The Republic of South Africa has a total chromite resource estimated at not less than 2

billion tons in the Bushveld complex in the Transvaal Province. Most of the material is friable and has a Cr_2O_3 content of 40 percent or more and a chromium-iron ratio or about 1.5 to 1. In Southern Rhodesia the reserves of the Great Dyke have been estimated to total 540 million tons, about one-third high-chromium and two-thirds high-iron, to a vertical depth of 500 feet on outcropping layers. Eluvial ores found adjacent to the Great Dyke may contain 60 million tons of concentrate. The total resource may be several thousand million tons. Other Rhodesian sources are the Selukwe, Mashaba, and Belingwe districts with a reserve estimated at some 8 million tons of high-alumina and high-iron ores.

Turkey long has been a major source of high-grade metallurgical chromite, but no definitive estimate of the total resource is possible. Geological inference suggests the probable existence of 10 million tons of shipping-grade ores and concentrates.

The Philippines have been the principal world source of high-alumina, refractory-type chromite for many years. The Coto ore body, northwest of Manila, is the largest deposit of this ore in the free world. The Acoje mine in Zambales Province, 10 miles north of the Coto deposit, has measured and indicated reserves of high-chromium ore exceeding 2 million tons. Other chromite deposits are distributed widely throughout the archipelago: Total reserves of refractory ore exceed 6 million tons; reserves of metallurgical ore in addition to the 2 million tons at Acoje are uncertain but probably not large.

Albania and Yugoslavia have produced metallurgical chromite consistently over the years from deposits along their common border, and reserves are estimated at about 500,000 tons for each country.

Little recent information is available concerning chromite reserves in the U.S.S.R., although the scale and high quality of recent exports imply a large reserve.

Chromite also occurs in Cyprus, Egypt, Finland, Greece, India, Iran, Japan, the Malagasy Republic, New Caledonia, Pakistan, Sierra Leone, and other countries.

TABLE 5.—*Estimated reserves and potential resources of chromite ore, by type and country* [1]

[Shipping ores and concentrates]

Country	Total, thousand long tons	High chromium [2]		High iron [3]		High aluminum [4]	
		Percent	Thousand long tons	Percent	Thousand long tons	Percent	Thousand long tons
South Africa, Republic of	2,000,000	5	100,000	95	1,900,000		
Southern Rhodesia	600,000	50	300,000	50	300,000		
Turkey	10,000	90	9,000			10	1,000
United States	8,000	5	400	92.5	7,400	2.5	200
Philippines	7,500	20	1,500			80	6,000
Finland	7,500			100	7,500		
Canada	5,000			100	5,000		
India	2,000	60	1,200			40	800
Malagasy Republic	2,000	100	2,000				
Cuba	1,500	10	150			90	1,350
Yugoslavia	1,500	100	1,500				
Iran	1,000	100	1,000				
Greece	750	50	375			50	375
New Caledonia	600	100	600				
Japan	500	50	250			50	250
Sierra Leone	150	100	150				
Brazil	150	100	150				
Pakistan	100	100	100				
Cyprus	100	100	100				
Other	1,000	60	600	20	200	20	200
Free world total	2,649,350	16	419,075	84	2,220,100	.04	10,175
U.S.S.R.	10,000	50	5,000			50	5,000
Albania	1,500	100	1,500				
World total	2,661,000	16	426,000	84	2,220,000	.06	15,200

[1] The figures for reserves and resources are intended primarily to indicate the relative importance of the countries, based on available information; upon further exploration and development some figures may be increased several times.

[2] Cr_2O_3, 45 percent or more; chromium-iron ratio, 2 to 1 or more; used mostly in metallurgy.

[3] Cr_2O_3, 40 percent or more; chromium-iron ratio, less than 2 to 1; used mostly as chemical ores.

[4] Al_2O_3, 20 percent or more; mostly used in refractories.

Source: Reference (5).

CONSERVATION PRACTICES

Growing acceptance of fines and concentrates by consumers has tended to promote utilization of lower grade ores and increased reserves proportionately. Reworking of waste piles has proven feasible in some instances.

Chromium ferralloy producers recover chromium from slag, and chemical processors rework residues and waste electroplating solutions. Chromium-bearing scrap alloys comprise part of the chromium added in new production of alloys.

SOURCES OF STATISTICAL INFORMATION

Domestic production, shipments, consumption, and stocks of chromite ore and concentrate; production, shipments, consumption, and stocks of chromium ferroalloys and chromium metal; and production and stocks of chromium chemicals (sodium bichromate equivalent) are compiled and published monthly by the Bureau of Mines. Chromium ferroalloys consumed in making steel and the quantity of chrome-bearing steels produced are compiled and published by the American Iron & Steel Institute.

Data on foreign exports and imports are published in the "Statistical Summary of the Mineral Industry, Overseas Geological Surveys" (London), in the "Statistical Yearbook of the United Nations" (New York), and in monthly and annual publications of various countries.

These data are adequate to meet most needs of government and industry, except that additional information on chromite reserves of the world by grades and data on present and projected consumption and uses in foreign countries are needed for estimating the quantity that will be available to the United States.

Export and import data on chromite and chromium products and the production of chromium chemicals are compiled by the Bureau of the Census, U.S. Department of Commerce. Under revised tariff schedules no attempt is made to distinguish between metallurgical-grade, chemical-grade, and refractory-grade chromite. The U.S. Tariff Commission's "Tariff Schedules of the United States, Annotated, 1963," effective September 1963, listed the following classifications for chromium ore imports:

601.1520 ..... Having a chromium content equivalent to not more than 40 percent chromic oxide (Cr_2O_3).

601.1540 ..... Having a chromium content equivalent to more than 40 percent but less than 46 percent chromic oxide (Cr_2O_3).

601.1560 ..... Having a chromium content equivalent to 46 percent or more chromic oxide (Cr_2O_3).

PRODUCTION, CONSUMPTION, AND TRADE

Since 1916, the United States has produced chromite mainly during emergency periods and in 1951–61, when the Government purchased chromite at incentive prices for stockpiling. Annual world production by countries from 1900 to 1958 was published in the Bureau of Mines Minerals Yearbook for 1958; data for succeeding years have appeared in annual editions of the Minerals Yearbook. Salient data for 1963 are given in table 6.

Data on world consumption of chromite ore are incomplete, but an approximation can be derived from estimates of world chromite production together with a relationship to world steel production. World chromite production in 1963 was estimated at 4,475,000 short tons and world production of steel ingots and castings at 425,310,000 short tons, averaging 21.0 pounds of chromite per ton of steel.

On this basis, 1963 consumption of chromite is estimated at 930,000 short tons in the U.S.S.R., 365,000 tons each in West Germany and Japan, 265,000 tons in the United Kingdom, and 205,000 in France. Consumption in the United States was higher than the 21.0-pound average, and consumption in other countries presumably was slightly lower.

In the United States, consumption of all types of chromite in 1963 was equivalent to about 26 pounds per ton of steel. This is a derived figure relating to end use consumption and was obtained by adding the computed ore equivalent of ferroalloys and metal consumed to ore consumed by the refractories and chemical industries.

TABLE 6.—*Salient chromite statistics*

[Thousand short tons and thousand dollars]

	1954–58 (average)	1959	1960	1961	1962	1963
United States:						
Production (shipments)	167	[1] 105	[1] 107	[1] 82	------	------
Value	$7,305	[2] $3,765	[2] $3,813	$2,939	------	------
Imports for consumption	1,805	1,554	1,387	1,329	1,446	1,391
Exports	1	11	5	5	3	10
Consumption	1,465	1,337	1,220	1,200	1,131	1,187
Stocks Dec. 31: Consumer	1,352	1,800	1,707	1,633	1,700	1,583
World: Production	4,310	4,315	4,885	1,660	4,840	4,475

[1] Produced for Federal Government only.
[2] Estimate by Bureau of Mines.

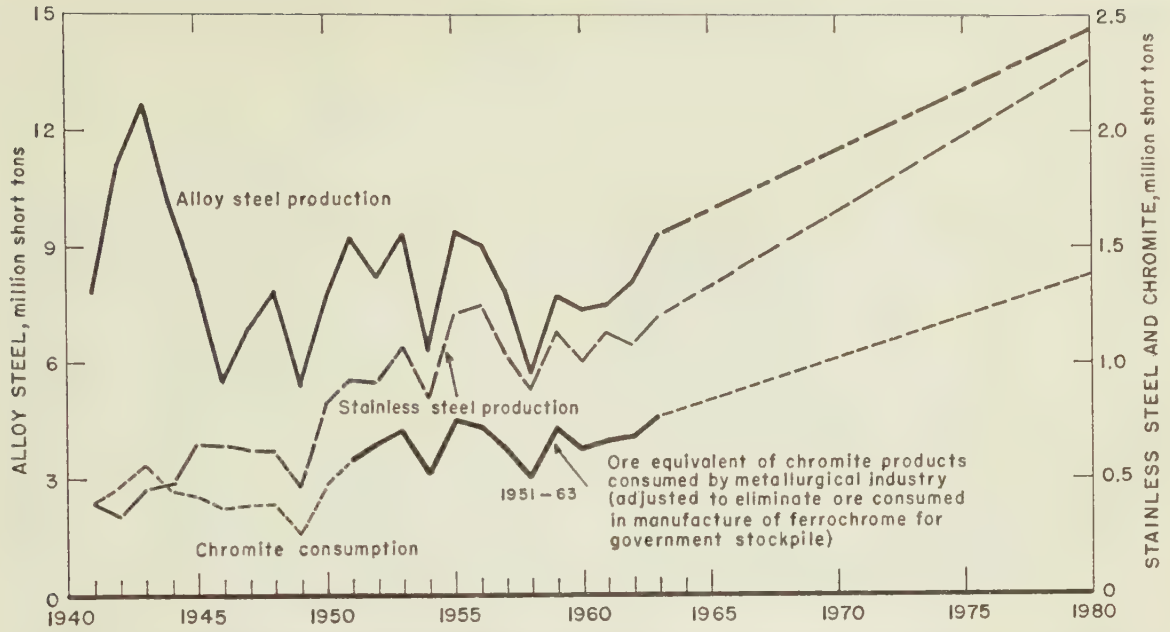

FIGURE 1.—Stainless and Other Alloy Steel Production and Chromite Consumption for Metallurgical Uses.

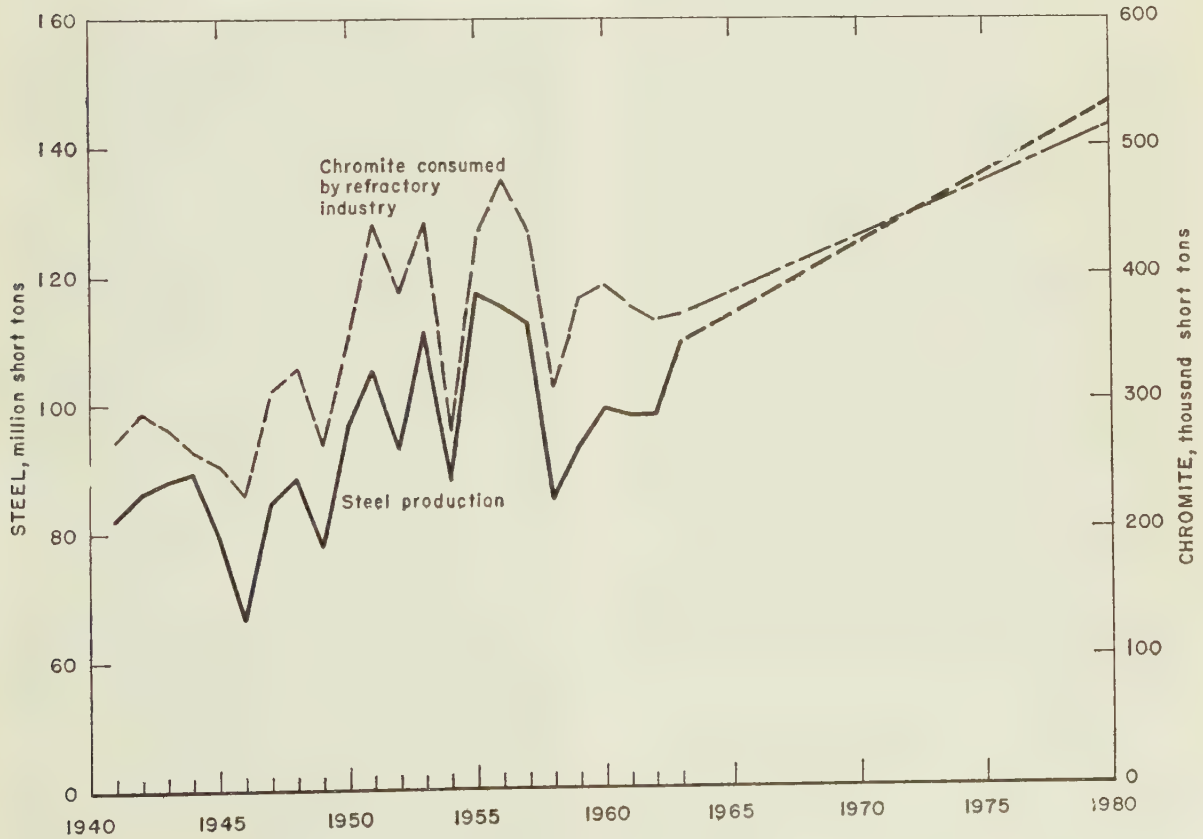

FIGURE 2.—U.S. Steel Production and Chromite Consumption for Refractory Uses.

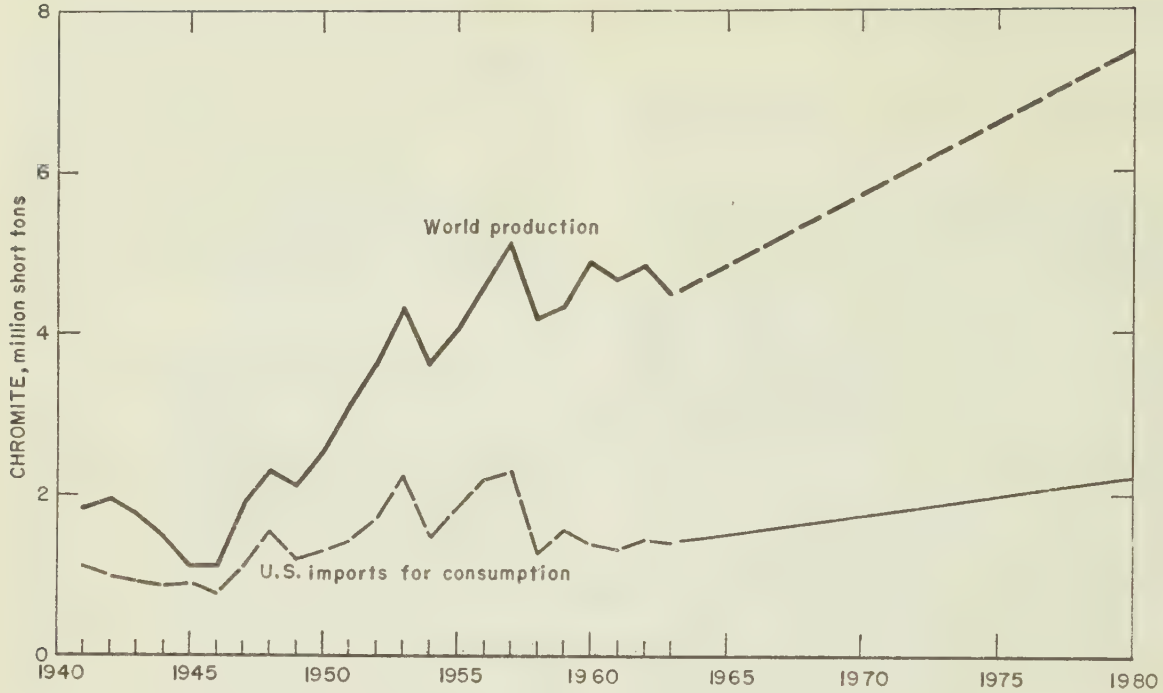

FIGURE 3.—World Production of Chromite and Imports to the United States.

Except for the U.S.S.R., industrial countries depend mainly on imports of chromite. In 1963, the world's new chromite supply came from the U.S.S.R. (30 percent), the Republic of South Africa (20 percent), Southern Rhodesia (9 percent), Albania (7 percent), and 13 other nations which produced the remaining 13 percent. Chromite imports comprised 100 percent of the new supply to the United States in 1962 and 1963 and virtually all except government stockpile purchases for the last decade.

In the 10-year period, 1954–63, imports from South Africa (30.4 percent), the Philippines (25.4 percent), Southern Rhodesia (19.9 percent), and Turkey (16.7 percent) comprised 92.4 percent of total U.S. imports. Imports from the U.S.S.R., after several years' suspension, were resumed in 1959 and comprised 14 percent of the total in 1963. No imports were received from Cuba in 1962 or 1963.

The United States has no import duty on chromite ores and concentrates. The Tariff Schedules of the United States, Annotated, 1963, effective September 1963, list duties as shown in table 7.

STRATEGIC CONSIDERATIONS

The United States is dependent on foreign sources for virtually all of its chromite. In 1956, the year of record domestic production, only 207,000 tons was produced and much of this was low in grade—purchased at incentive prices under the Government stockpiling program. Nevertheless, the resource conceivably could supply 5 to 10 percent of the Nation's needs under sufficiently critical emergency conditions.

The long sea lanes between the United States and its major sources in the Philippines, Turkey, the Republic of South Africa, Southern Rhodesia, and in recent years the U.S.S.R., present serious transportation problems during war. Rail transportation from mines and mills in the Western United States to processing plants in the East is costly and could be in short supply during an emergency. However, the Western United States is not a major source of supply. More important are the limited facilities for moving chromite from mine to port, and limited port loading facilities, in some of the major producing countries.

In Turkey, much of the high-grade metallurgical ore is hauled from mine to port by motortruck, and in past shortages of tires and spare parts have curtailed shipment. In South Africa, according to Greathead (*6*):

> The Eastern Belt is poorly served by only two rail-loading points, Burgersfort and Steelpoort, 11 miles apart by road, and mines more than 30 miles from them have not been worked to any extent. The distances from these railheads to the nearest port Lourenço Marques, are 336 and 351 miles, respectively.

TABLE 7.—*Rates of duty on chromium imports to the United States*

[Duty is assessed per pound]

Item	Article	Rates of duty	
		Free world [1]	Communist areas [2]
420.08	Potassium chromate and dichromate	2.25 cents per pound	2.25 cents per pound.
420.98	Sodium chromate and dichromate	1.75 cents per pound	1.75 cents per pound.
422.92	Chromium carbide	12.5 percent ad valorem	25 percent ad valorem.
473.10	Chrome green	10 percent ad valorem	Do.
473.12	Chrome yellow	do	Do.
473.14	Chrome oxide, green	do	Do.
473.16	Hydrated chromium oxide green	do	Do.
473.19	Strontium chromate	do	Do.
531.21	Chrome bricks	25 percent ad valorem	Do.
601.15	Chrome ore	Free	Free.
607.30	Ferrochromium not containing over 3 percent by weight of carbon.	8.5 percent ad valorem	30 percent ad valorem.
607.31	Ferrochromium containing over 3 percent by weight of carbon.	0.625 cent per pound on chromium content.	2.5 cents per pound on chromium content.
607.55	Ferrosilicon chromium	10 percent ad valorem	25 percent ad valorem.
632.18	Chromium metal	10.5 percent ad valorem	30 percent ad valorem.

[1] Duties apply to imports from countries other than U.S.S.R. and other designated communist areas.
[2] Duties apply to imports from U.S.S.R. and other designated Communist areas.

Rail facilities in the Western Belt are far better; although the distances to Lourenço Marques range from 380 to 490 miles. The road distances to the railheads from the present working mines vary from 2 to 18 miles.

In 1960 the Rhodesian industry and the railway system reportedly were geared to produce and export well over 1 million tons per year. However, the mines are more than 500 miles from either the Lourenço Marques or the Beira seaports, both in Mozambique.

U.S. Government stockpiles on June 30, 1964, totaled 8.0 million short dry tons, of which 5.5 million was metallurgical-grade chromite, 1.3 million chemical-grade chromite, and 1.2 million tons was refractory-grade chromite. Some of the material included in the above totals had been converted to ferrochromium or other products.

Chromite-consuming plants in the United States are dispersed so that they do not constitute an unusual protection problem.

GOVERNMENT PROGRAMS

Government policy was an important factor in domestic production between 1951 and 1961, when virtually the entire output was purchased at incentive prices under the Defense Production Act of 1950. Foreign chromite ores, chromium ferroalloys, and metal have been acquired through the exchange of surplus agricultural products.

To encourage exploration of domestic chromite deposits, the Office of Minerals Exploration offered assistance to private industry in the amount of 50 percent of the approved estimated cost. The moneys were to be repaid from production. This program was initiated in 1959 and was still in effect in 1963.

PRICES

Prices are determined by negotiation and no fixed standard applies either to base prices, premiums, or penalties. Sales of refractory ores are based on known refractory characteristics of ore from a specific source. Sales of metallurgical and chemical ores are based on chromic oxide content, impurity constituents, and the lumpy or friable nature of the ore. Lumpy ore with a 3 to 1 chromium-iron ratio is desired for most metallurgical uses. Friable ore is preferred for chemical use, and low silica content is desirable in all uses.

Average annual prices have ranged from about $10 per long ton (eastern seaboard) in 1921 to about $56 in 1957.

Published prices in 1963 were listed for the most part as nominal. Although some as low as $16 were rumored, these undoubtedly applied to fines or other less desirable materials. Prices for standard grades of metallurgical ore, in the United States, probably were in the range of $24 to $26 throughout most of 1963.

Chromium ferroalloys are sold in the United States by the pound of contained chromium and the prices vary according to composition and quantity. Prices quoted by E&MJ Metal and Mineral Markets at the end of 1963 for ferro-

chromium in carload lots f.o.b. shipping point follow:

	Cents per pound
High carbon 67 to 71 percent Cr, all grades carbon	19
Low carbon 67 to 73 percent Cr, 0.025 percent carbon	24½
67 to 71 percent Cr. 0.05 percent carbon	23½
Charge chrome 61 to 66 percent Cr, 5.5 percent carbon	13½
Refined chrome 61 to 68 percent Cr, 4.25 percent carbon	22

TAXES

Producers of chromite ore and concentrate are granted a depletion allowance of 23 percent on income from domestic production and 15 percent on income from foreign production. In addition to the 15-percent depletion allowance, taxable income of operations outside the United States and within the Western Hemisphere is taxed at a lower rate, 14 points below the U.S. corporate income tax rate.

RESEARCH

Chromium resource investigations have included widespread search for ores, examination of deposits, and efforts to develop concentrating and utilization procedures for low-grade ores.

During World War II, Bureau of Mines and Geological Survey engineers and geologists investigated all known chromite sources in the United States to reduce the Nation's dependence on ocean transport. Under the Defense Production Act of 1950, financial assistance in exploration was offered through the Defense Minerals Exploration Administration (now the Office of Minerals Exploration); and a purchase program, through the Emergency Procurement Service of the General Services Administration, offered incentive prices to domestic chromite producers. Both of these programs stimulated widespread search and resulted in some production but brought little actual increase in total reserves.

Bureau of Mines scientists have conducted a number of studies on utilization of low-grade chromites. Mechanical and chemical methods of concentrating and smelting procedures for converting low-grade concentrate to usable ferrochromium have been investigated (*9–11*, *15*, *20*). A pilot plant, operated by American Chrome Co., Nye, Mont., produced as much as 13 to 14 tons per day of chromium ferroalloy from Montana chromite. Operations started in December 1958 and ended in 1961 (*8*).

Industry has made significant contributions to the more efficient use of chromium through the development of alloys, through improved smelting and fabricating techniques, and throughout the range of chromium or chromite applications. Improved electroplating techniques, development of catalysts, and adaptation of South African chromite for refractory use are noteworthy research accomplishments.

OUTLOOK

Major changes in the supply and use patterns over the next 10 to 20 years will involve increasing use of fines and concentrates, increasing interchangeability of use between the different chromite ore types, and increasing reliance on a relatively few large sources. Known world reserves of metallurgical- and chemical-grade chromite are more than adequate for many decades, but reserves of refractory-grade, high-alumina ores will be seriously depleted within 10 years.

Chromite resources in the Western Hemisphere will have little significance in the foreseeable future. In the next 10 to 20 years Rhodesia and the Republic of South Africa will gain in importance, while other traditional free world sources will supply a diminishing proportion of world requirements. The U.S.S.R. may continue as a major source of free world supply for decades, but subject to uncertainties regarding reserves and possible changes in governmental policy.

The major use of chromium by the domestic metallurgical industry is in stainless steel. The trend in stainless production relative to total steel (1950–63) suggests that by 1980, stainless may comprise 1.6 percent of total steel output, or about 2.3 million tons of the projected 147-million-ton total. This will require the equivalent of 1.0 million tons of chromite averaging about 48 percent Cr_2O_3. Other alloys will consume an additional 0.4 million tons, assuming continuation of the 1963 ratio. Thus the total consumption in 1980 by the domestic metallurgical industry will be about 1.4 million tons of chromite. Any shift to lower grade ores such as the 44 percent Transvaal ores will call for a corresponding increase in tonnage.

Consumption of chromite per ton of total steel, by the refractory industry, showed a slight downward trend in 1959–63, and the growing use of oxygen in steel production will accentuate this trend. However, assuming 3.5 tons of chromite per 1,000 tons of steel, consumption will increase from 368,000 tons of chromite in 1963 to more than 500,000 tons in 1980.

Based on anticipated growth rates for population (1.6 percent), labor force (1.6 percent),

and gross national product (3.8 percent), a growth rate of 2.0 percent for the chromium chemicals industry is assumed. This will increase consumption from 187,000 tons in 1963 to about 250,000 tons in 1980. Overall projected figures for 1980 are:

	Million tons
Metallurgical industry	1.4
Refractory industry	.5
Chemical industry	.25
Total	2.15

As a basis for comparison, about 26 pounds of chromite (all types) was consumed in 1963 per ton of steel produced by the domestic industry. Of this total, about 15.1 pounds was consumed by the metallurgical industry, about 3.4 pounds by the chemical industry, and about 7.5 pounds by the refractory industry. If applied to the projected 147-million-ton steel production of 1980, these factors would indicate a total U.S. chromite consumption of 1.91 million tons.

Imports of chromite (all types) to the United States in 1963 comprised 31 percent of world production. This was approximately the ratio of U.S. steel production to world steel production (25.7 percent) in the same year, and on this basis world demand in 1980 is estimated at three to four times the domestic requirement, or 6 to 8 million tons.

PROBLEMS

Almost complete dependence on foreign sources is the underlying cause for many of the supply problems faced by U.S. industry and defense planning agencies. These include price fluctuation, transportation problems, government instability in some areas, stockpile acquisition and storage problems.

Depletion of some traditional sources and the trend to interchangeable use of various chromite ore types present technical and economic problems to producers and consumers.

The brittle behavior of chromium metal and related problems in fabrication have restricted its use in some applications where its oxidation resistance might otherwise be used to advantage.

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CLAYS

By James D. Cooper [1]

CLAY minerals are hydrous aluminum silicates, which are mixed in nature in varying proportions yielding a variety of clay types. The principal industrial clays are kaolin, ball clay, fire clay, bentonite, fuller's earth, and miscellaneous clay. About 57 percent of all industrial clay produced is used in manufacturing formed ceramic and refractory products and 34 percent in production of cement and lightweight aggregates; the remainder is used for fillers and numerous miscellaneous applications.

The total clay sold and used in the United States in 1963 was 50.2 million short tons valued at $181 million. Before World War I imported clays, particularly kaolins and ball clays, constituted an important part of the clay industry; now imports constitute only a small fraction of 1 percent of total U.S. consumption. The reverse trend has taken place with exports; formerly very little clay was exported, but since 1945 the exports have increased. The quantity exported is less than 2 percent of production but equivalent to nearly 12 percent of the value.

Georgia, Utah, and South Carolina are the main producing States for kaolin; Kentucky and Tennesse, for ball clays; and Georgia and Florida, for fuller's earth. Wyoming, South Dakota, Mississippi, Texas, and Arizona are the chief areas of bentonite production. The major part of production of fire clays is from Ohio, Pennsylvania, and Missouri, but there is substantial production from a number of other States. Miscellaneous clay is produced in all States except Alaska and Rhode Island.

Kaolin is used principally for paper and rubber fillers, refractories, and whitewares. Ball clay is used principally for whiteware, floor and wall tile, and refractories. Fire clay is used for refractories, heavy clay construction products and stoneware. Bentonite is used in foundry sands, drilling muds, absorbents, and iron ore pellets. Miscellaneous clay is used for heavy clay products, cement, lightweight aggregate, and in refractories and stoneware.

Specifications and tests vary with the type of clay and its properties and uses. Significant properties in ceramics are particle size, plasticity, fired color, strength, shrinkage, porosity, density, vitrification range, deformation temperature, bloating characteristics, and others. Properties important for nonceramic uses include: for the fillers—freedom from grit, particle size, color, and texture; for oil clarification—decolorizing ability and oil retention.

Until recent years methods of control and evaluation of clay properties were largely empirical, and simulated service tests often were cumbersome and time consuming. With increasing production and demand for better products the need for more precise controls and manufacturing procedures has brought about intensive research in governmental, educational, and private institutions. Study of the fundamental crystalline structures, effects of impurities, and other factors has revolutionized concepts and resulted in better scientific controls and tests.

The outlook is for increasing demand for better refractory and ceramic materials. Total clay production and consumption will continue to increase at a somewhat lower rate than gross national product (GNP), but individual classes of clay will not necessarily follow the same growth pattern because of changing technology, new uses, and changes in architectural styles.

[1] Commodity specialist.

BACKGROUND

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Because of the widespread occurrence of brick and pottery clay there are few areas of the world that do not have some sort of clay industry. In the United States 50.2 million tons of clay, valued at $181 million, was produced in 1963 from 1,300 mines by about 1,000 firms. Almost 900 of these firms produce miscellaneous clay used principally for heavy clay products (building brick and tile, sewer pipe, and terra cotta) lightweight aggregates, and portland cement, or fire clay, for use in refractories and heavy clay products. The U.S. clay industry employs about 4,500 in mine production and approximately 150,000 in processing and manufacturing clays and clay products. In 1963, about 97 percent of all miscellaneous clay and 70 percent of fire clay mined in the United States was from mines owned or controlled by consumers. Essentially all of the bentonite, fuller's earth, kaolin, and ball clay produced in 1963 was mined by about 90 firms in 24 States, primarily engaged in mining and preparing the materials for the market.

Georgia and South Carolina, for many years the major producers of kaolin, supplied about 94 percent of the total annual output during 1959–63. Production was reported from eight other States. Most of the domestic ball clay production in this same period, came from western Tennessee and Kentucky, with smaller quantities reported from California, Maryland, and Mississippi.

During 1959–63 fire clay output was reported from 29 States. Ohio, Pennsylvania, Missouri, and Texas, in that order, were the major producers, supplying about 65 percent of the total.

Bentonite production in 1959–63 was principally from Wyoming, Mississippi, and Texas; fuller's earth was produced mainly in Florida, Georgia, Mississippi, and Tennessee.

Miscellaneous clay and shale were produced in nearly all States and in 1959–63 furnished about 71 percent by quantity and 25 percent by value of the total domestic clay production.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Clays are earthy mineral aggregates consisting essentially of hydrous aluminum silicates which are plastic when sufficiently pulverized and wetted, rigid when dry, and vitreous when fired at a sufficiently high temperature. The term clay is sometimes loosely used for all fine grained material—about 2 microns or less—regardless of plasticity.

Shales used in the ceramic industry are products of consolidation of clays under pressure. When pulverized and wetted, these shales become plastic or otherwise regain the characteristics of clays.

Types of Clays

Clays are classified in six groups in Bureau publications. These are kaolin, ball clay, fire clay, bentonite, fuller's earth, and miscellaneous clay.

Kaolin is a mineralogical term referring to a clay in which the predominant clay mineral is kaolinite. China clay is used synonymously with kaolin. Halloysite, although differing somewhat in chemical composition and lattice structure, is included under kaolin in Bureau statistical reports. Commercial kaolins have a nearly white dry and fired color. Grades of kaolin are determined by intended uses in whitewares, rubber, paper, refractories, and other products. Specifications are based on the method of preparation (crude, air separated, water washed, air dried, spray dried, slip, pulp, slurry, or water suspension) and on specific physical and chemical properties.

The term ball clay originated from the unusually high plasticity of clays so named, which enabled them to be rolled readily into balls. In early mining practice, mostly by hand labor, the material was rolled into balls, then thrown into wagons. Ball clays consist principally of kaolinite, but have a higher silica-to-alumina ratio than is found in most kaolins as well as larger quantities of mineral impurities and much organic material. They are usually much finer grained than kaolins and, in general, set the standards for plasticity. The fired products are generally not as white as those made of kaolins.

Specifications for ball clays are based on methods of preparation (crude, shredded, air floated) and pertinent physical and chemical tests, which are much the same as those for kaolin (*6*, *24*).[2]

The terms "fire clay" and "stonewear clay" are based on usage—fire clay indicating use for refractories, and stoneware clay indicating use for such items as crocks, jugs, and jars. Fire clays are basically kaolinitic but usually include other clay minerals such as halloysite and illite, and both organic and inorganic impurities. In-

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

cluded under the general term fire clay, are the diaspore, burley, and burley-flint clays. Diaspores are largely aluminum hydrates ($Al_2O_3 \cdot H_2O$). The burley clays contain burls (oölites or nodules) and are varieties of diaspores with some halloysite and kaolinite. The burley flint clays contain small oölites predominantly of halloysite, with some kaolinite and diaspore. The fired colors of fire clays range from reds to buffs and greys.

Based on relative plasticity and hardness, the following types of fire clay are recognized by the trade: Plastic, semiplastic, semiflint, flint, and nodular flint. Several recognized types also are defined according to use: Among these are stoneware, tile, refractory, and heavy-clay-product clays. Specifications are based on pertinent physical and chemical tests of the clays, and of products made from them (*24*).

Bentonite was named from a deposit in the Fort Benton shale in Wyoming, where the material was first recognized as a separate type of clay. Bentonites are composed essentially of minerals of the montmorillonite group. Two types are recognized—the swelling and nonswelling (meta- or sub-bentonites). The swelling type is the only clay that will increase materially in volume when wetted with water. It is high in sodium, whereas the nonswelling types are high in calcium. Standard grades of swelling bentonite increase from 15 to 20 times their dry volume. Foundry sands and drilling muds compose the two main grades of the swelling types. In recent years iron ore pelletizing has grown rapidly, requiring large quantities of the swelling bentonite as a binder. Nonswelling bentonites are used for bleaching, filtering and catalysis by the petroleum industry, and in foundry sands. The specifications are based on pertinent physical and chemical tests, particularly those relating to particle size and swelling index (*1, 4, 40, 44*).

The term "fuller's earth" is derived from the first major use of the material, which was for cleaning textiles by fullers. Fuller's earths are essentially montmorillonite or attapulgite. The montmorillonite fuller's earths closely resemble sub-bentonites and tend to be high in magnesium (*33*). Fuller's earths have almost the same grades as those of nonswelling bentonites, except that they are not used in foundry sands. An additional important grade is that of absorbent (floor sweep). Specifications are based on the physical and chemical tests of the products (*3, 24*).

The term "miscellaneous clay" is a statistical designation used by the Bureau to refer to clays and shales not included under the other five clay types. Miscellaneous clay may contain some kaolinite and montmorillonite but illite usually predominates, particularly in the shales. There are no specific recognized grades based on preparation, and very little based on usage, although such a clay may sometimes be referred to as common, brick, sewer pipe, or tile clay. Specifications are based on the physical and chemical tests of the products (*7, 24*).

Specifications

Specifications of clays are based on end uses. Although many specifications have been established by the American Society for Testing and Materials (*5, 6, 7*), American Foundrymen's Association (*1*), American Oil Chemists Society (*3*), American Petroleum Institute, Technical Association of the Pulp and Paper Industry (*46*), and other national organizations, many producers and consumers rely on their own tests and specifications applicable to their specific needs (*24*). The tolerance limits of mineralogical composition, particle size, and other physical and chemical properties also are determined largely by individual requirements.

For use in ceramic wares, the important properties are plasticity, fired color, dry and fired strength, drying and firing shrinkage, and the vitrification range (the range of temperature at which, for a given method of forming and schedule of firing, minimum volume and porosity are maintained without appreciable change).

For refractory uses, the most significant single property is the pyrometric cone equivalent (PCE), which is determined by comparing the softening behaviour of a clay sample subjected to a standard time-temperature schedule with that of standard cones. Clays having a PCE of 33 (3,169° F at 270° F heating rate per hour), or higher are used for manufacturing superduty refractories; those with a PCE of 31 (3,061° F) up to 33, for high-duty refractories; and those with a PCE of 30 (3,029° F) up to 31, for low-duty refractories. Serviceable refractories for some purposes can be made from clays having a PCE as low as 15 (2,606° F).

Clays for refractories not only must have an acceptable PCE but also when made into standard refractory brick by commercial forming processes, must meet high-temperature load and spall tests (ASTM Designations C–16 and C–122, respectively) (*7*). These tests, as well as many other ceramic end-product tests that reflect the properties of the raw materials used, are time consuming, cumbersome, and expensive.

Clays or shales (and slates) for producing thermally expanded lightweight aggregate must become pyroplastic and full of fine gas bubbles when heated to the appropriate temperature

range, preferably 1,800° to 2,200° F. Nonexpandable clays and shales are used in production of lightweight aggregates by sintering clay mixed with coal or other combustible materials that will burn out, leaving voids.

Clays used in manufacturing cement are selected to supply deficiencies in chemical composition, such as silica, iron oxide, and alumina not present in the available limestone or cement rock.

The most desirable clays for rotary-drilling muds are those which swell when wetted with water.

Filtering and decolorizing clays have high sorption such as characterize the montmorillonite and attapulgite groups of minerals.

For filler clays and paper coating clays, emphasis is on fineness of grain and whiteness of dry, unfired clay; for insecticide carriers high adsorption is important.

TECHNOLOGY

Mineralogy and Geology

Natural clays consist of many different minerals, but certain minerals or classes of minerals occur in all clays and are called clay minerals. Mineralogically the clay minerals have been classified as hydrous aluminum and magnesium silicates. The names, chemical composition, and optical properties of these silicates are given in table 1.

Of the clays used by the ceramic industry the kaolin group is the most prevalent. Kaolinite, halloysite, dickite, and nacrite are the principal minerals in this group.

The montmorillonite minerals are less common than kaolins but comprise an important group of clay minerals. With the addition of water, some minerals of this group swell, resulting in increased volume. The best known example of this phenomenon is the swelling bentonites. Montmorillonite, nontronite, and volchonskoite form one series where silica, alumina, magnesia, iron oxide, and water are the principal components. Volchonskoite contains about 15 percent chromium oxide, Cr_2O_3. Saponite and hectorite make up another series containing chiefly magnesia, lithia, silica, and water. Illite represents an important but not too well understood mineral group.

The magnesium silicate group of palygorskite (attapulgite) and sepiolite is much less common than the other groups. The minerals are essentially hydrated magnesium silicates.

Geologically, clays are of two general types—residual and transported; but in all instances clay is of secondary origin, having been formed by the alteration of other rocks. Clays may be found in a variety of forms—as a soft paste, soft solid (mudstone), or as laminated rock (shale). They may occur at or near the surface or at relatively great depths. The kaolinitic clays of commerce are derived largely from feldspathic rocks and the bentonites and fuller's earths from volcanic ashes. The decomposition is usually a result of weathering, although hydrothermal reactions are responsible in many instances. Shales and flint fire clay are clays that have been compacted and hardened by metamorphic processes.

Some china clay and bentonite deposits are formed by weathering of rocks in place, but most commercial deposits have been transported.

TABLE 1.—*Physical properties of the clay minerals* (*33*, *42*)

Name	Composition	Optical properties							
		Crystal system	Specific gravity	Hardness	Refractive index	Birefringence	Interference figure	Crystal habit	Color
Kaolin group:									
Kaolinite	$Al_2(Si_2O_5)(OH)_2$	Triclinic	2.61	2.0	1.56	0.006	B-neg	Plates	None.
Halloysite	$Al_2(Si_2O_5)(OH)_2$	Hexagonal(?)	2.62		1.52	.030	do	Small needles.	Do.
Livesite	$Al_2(Si_2O_5)(OH)_2$	Monoclinic	2.63		1.54	.020	do	Small plates.	Yellow(?).
Dickite	$Al_2(Si_2O_5)(OH)_2$	do	2.62	2.5	1.56	.006	do	Plates	None.
Nacrite	$Al_2(Si_2O_5)(OH)_2$	Orthorhombic	2.54	2.5	1.56	.006	B-neg(?)	do	Do.
Anauxite	$Al_2O_3 3SiO_2 2H_2O$		2.60						
Allophane	$Al_2O_3 \cdot nSiO_2 nH_2O$				1.49		Isotropic		
Montmorillonite group:									
Montmorillonite	$(Al,Mg)_2Si_4O_{10}(OH)_2$	Monoclinic	2.50	2.0	1.51	.021	B-neg	Small flakes.	None.
Nontronite	$(Al,Fe,Mg)_2(Al,Si)_4O_{10}(OH)_2$	do	2.60	2.0	1.56	.023	do	Small laths.	Brown.
Hectorite	$(Mg,Li,Al)_3Si_4O_{10}(OH)_2$	do	2.4	2.0	1.49	.022	do	Small flakes.	None.
Saponite	$Mg_3(Al,Si)_4O_{10}(OH)_2$	do	2.5	2.0	1.50	.015	do	do	Do.
Hydromica (illite)	Variable	do	2.75		1.57	.021	do	Plates	Do.
Magnesium silicate group:									
Sepiolite	$H_4Mg_2Si_3O_{10} \cdot nH_2O$	Orthorhombic	2.0	2.0	1.53	.010	U-neg	Small fibrous.	Do.
Palygorskite(attapulgite)	$Mg_5Si_8O_{20}(OH)_2 \cdot 8H_2O$	do			1.51	.020		do	

Mining

Most clays and shales are mined by open-pit methods. Some deposits are mined by underground methods, usually room-and-pillar, through adits or inclined shafts. Steeply dipping refractory clay beds east of the Front Range in Colorado are mined by shrinkage stoping. Hand methods are still used at many small mines. In recent years improvements in earth-moving equipment have greatly extended the economic depth of surface mining. For example, many of the northern Missouri fireclay deposits that up to a few years ago were mined by underground methods are now being operated as open pits, with overburden-to-clay ratios as high as 10:1.

Some kaolin deposits are mined by hydraulicking. The clay is washed down by jets of water and the clay-water suspension is raised to the surface by pumping or in bucket elevators. It may move from the surface to the refining plants by gravity flow or by pumping. Kaolin slurries are sometimes pumped substantial distances (10 to 12 miles). The usual procedure in Georgia is to collect the material at a blunger (mixer) near the mine, add a deflocculant, and then pump the slurry to the refining plant. In one plant a primary portable blunger is used at the pit before the main blunger. Rubber-lined conduit is used.

Little blasting is required in clay or shale mining, except in some fire clay mines. Shale planers are used at some open-pit mines. Transportation of mined clay to plant bins or stockpiles is usually by truck, but conveyor belt or railroad transportation is used where applicable.

Processing

Kaolin

Kaolin may be marketed after crushing and screening or air separation. More often, after preliminary crushing and screening, sand, mica, and other impurities are separated by sedimentation in water and the clay is then recovered by thickening, followed by filter-pressing and heated air drying. Within the last decade, however, spray drying has largely superseded the filter press, particularly for paper fillers and coaters. After bleaching with sulfurous acid the material is spray dried. Some kaolin for enamel, paper coating, and other usage is reduced to such fine particles that only a small percentage of the total production exceeds 1 or 2 microns in maximum dimension.

The coating clays differ essentially from most filler clays in grain size, and additional bleaching is usually required. The filler and coater portions of a clay are separated by classification sizing, the very fine being coater, the coarser being filler. In some clays the proportion of grain fine enough for coater is comparatively small. Conventional fine grinding and micronizing are relatively costly. An experimental grinder and process developed by the Bureau has shown considerable promise for production of coating clay from low-grade material, and a number of the kaolin producers have built similar grinders and are continuing to refine the process.

Paper clays after spray drying are loaded directly into covered gondola cars for shipment. Formerly, these clays were shipped mostly in tank cars as slurry containing about 70 percent solids, or as dry clay, in bulk, in lined boxcars. For ceramic purposes, dry clay is usually ground and bagged for shipment but is sometimes transported in lump bulk form.

Ball Clay

Ball clay from the pit usually is dumped into a shredder, consisting of a bowl suspended over a revolving slotted plate to which knives are attached. The weight of the clay forces it against the knife, and as each piece is cut off it drops through the slot to a belt and is delivered to storage.

Ball clays are shipped as air-dried lump clay, air-dried shredded clay, semidried shredded clay, or dried pulverized and air-floated clay. Semidried ball clay is obtained by processing in rotary driers. Coarse sand and lignite are removed by air separation. Lump and shredded ball clay usually is shipped in bulk, and pulverized and air-floated ball clay is shipped in bags.

Fire Clay and Miscellaneous Clay

Primary crushing of fire clay, miscellaneous clay, and shale usually is done with jaw or gyratory crushers, rolls, or hammer mills. For ceramic products, secondary crushing and grinding are quite generally by dry pan, occasionally by wet pan. Dry and wet pans are similar to chaser mills. Dry pans operate continuously and discharge the crushed clay through a screen bottom. In wet pans batches of clay or shale are ground with water to the desired consistency. Secondary crushing is usually followed by screening. A rotary drier sometimes is used ahead of the screens. After crushing and screening the material may be fed into a pugmill and an extrusion machine. Where dry presses are used in making the final product, the crushed and screened material is fed into mixers and then directly to the press.

Clays and shales used for production of lightweight aggregate by the rotary kiln method are usually crushed to the proper size, screened, and fed to storage hoppers or directly to the kilns. Fines from the crushing operation may be utilized by pelletizing, or in some cases by allowing clay fines to recompact by natural weathering. At some plants the fines are wasted.

In the sintering furnace method the clay or shale is pelletized, usually with the addition of coal dust or other combustible material, and the pellets passed through an ignition zone where the combustibles are burned out, causing partial fusion of the clay, and leaving voids which account for the low weight.

The sintered material and much of the rotary kiln aggregate, is crushed to the required sizes for use in concrete.

In the cement industry primary crushing is the same as for structural clay products. Secondary crushing and grinding is done in ball or rod mills to insure the necessary fine grain (minus 200-mesh), after which the material is screened and ready for the rotary kiln. Both wet and dry processing are used.

Bentonite

Preparation of bentonite consists of drying, with care to avoid overheating, and grinding by ball, rod, or roller mills to specific sizes, including air-floated material. About 10 sizes are marketed, ranging from 20-mesh to minus 1,500-mesh. Most bentonite is shipped in bags.

Fuller's Earth

Fuller's earth is processed by feeding directly to a single-roll crusher as it comes from the mine. The screened material is conveyed to storage bins, then fed by mechanical feeders into pugmills. The clay is extruded from the pugmills through perforated steel plates into rod or spaghetti-like forms from ½- to ¾-inch diameter. The extrusions are conveyed to a rotary dryer. From the dryer the clay is screened to pass 8-mesh, the undersize going to a series of three bolting machines (steel-roll and sifter combinations) with provision for recirculating the oversizes. These bolting machines are the same as those used in flour mills. Each roll mill grinds a little more of the clay to the desired sizes, and each sifter separates the oversize from the market products which are minus 15-, plus 30-mesh; minus 30-, plus 60-mesh; minus 60-, plus 90-mesh; and minus 90-mesh. Fuller's earth for insecticide use is ground in roller mills. Fuller's earth used for floor sweep is calcined in rotary kilns and screened to eliminate particles finer than 16-mesh. Fuller's earth is shipped in bags.

USES

Clays may be used in the raw or unfired condition or as a fired product. Color, texture, bonding strength, and absorptive qualities of the clay govern its use as an unfired material. Some of the major uses of fired clays are as refractory, structural, and decorative materials. The names given to certain types of clay such as china, brick, stoneware, or terra cotta refer only in a general way to their properties. A clay suitable for brick can be used to make drain tile. Clay products such as architectural terra cotta and chemical stoneware are usually made from mixtures of clays. Whiteware bodies contain kaolin, ball clay, talc, quartz, and feldspar.

The paper, rubber, refractories, and pottery industries are the principal kaolin consumers. The paper industry, which utilizes kaolin both as a filler and coater, is the largest single consumer, using half of the total output. Chemicals, cosmetics, insecticides, petroleum catalysts and miscellaneous uses account for about 8 percent of the total.

Pottery, stoneware, and floor and wall tile are the major uses of ball clay. Refractories, art pottery, saggers, and kiln furniture require smaller quantities.

Fire clay is used primarily in heavy clay products and refractories, which take approximately 95 percent of the total output. Fillers, drilling muds, and chemicals account for most of the remainder.

More than 55 percent of the bentonite production goes into rotary drilling muds and foundry sands and facings. The most important new use is as a bond in pelletizing iron ore concentrate.

Absorbents, insecticides and fungicides, and drilling muds, in that order are the major products requiring fuller's earth. These uses take about 85 percent of the annual output.

Heavy clay products such as building brick, sewer pipe, drain tile, and similar products take more than 50 percent of the output of miscellaneous clay. Portland cement and lightweight aggregate are the other major products requiring this type of clay, with less than 2 percent going to other uses.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Mica, silica sand, and bauxite are obtained as byproducts or coproducts in processing kaolins. Some of the sand produced is suitable for building materials. The mica is of the type used in producing ground mica. No byproducts or coproducts are obtained from other types of clays.

Coal-measure clays or shales, however, are sometimes mined in conjunction with coal.

Clays have many commercial and technological relationships to other mineral commodities. In some of these interrelated industries, clays occupy a primary function in manufacturing finished products, for example, cement, lightweight concrete, and drilling muds. In others clay may be only one of several satisfactory raw materials available. The quantities of kaolin and ball clay used in the production of whiteware affect the demand for feldspar, ground silica (potter's flint) and various other mineral components. There is also an interdependence of the fire-clay refractories industry and the metallurgical industries.

High-alumina clays (fire clay and kaolin) are a potential source of alumina for aluminum production, but costs are too high for clay to compete with bauxite for this purpose in the United States. In 1958, however, The Anaconda Company began operating a 50-ton-per-day pilot plant in Anaconda, Mont., to produce aluminum-grade alumina from the clay of Latah County, Idaho, and in 1963 aluminum was produced on an experimental basis in two pots using alumina produced from Latah County clay. Also in 1963 several thousand tons of Georgia kaolin was shipped to Anaconda for experimental alumina production.

Clay or shale is utilized to balance the alumina and silica content of the raw-material mix at many cement plants.

Fire clay and kaolin have a complex relationship with a wide variety of other refractory materials, including silica, dolomite, mullite, magnesite, chromite, graphite, pyrophyllite, bauxite, olivine, silicides, carbides, nitrides, borides, and rare-earth oxides. Considerations governing the selection of a specific refractory, in addition to PCE, are bonding qualities, load-bearing strength under operating temperatures, and resistance to spalling and slagging. The relationship of refractory clays to bauxite is close, as many refractory products are made from mixtures of clay and bauxite.

ALTERNATE MATERIALS

For ceramic purposes there are no direct substitutes for clays, although there are alternate materials for almost all clay products. Wood, glass, concrete, plastics, various metals, and other materials may be used in place of ceramic clay products.

For most nonceramic uses there are alternate materials. For example, carbon black has replaced clay to some degree as a filler in rubber for tires and certain other rubber products. Several materials, such as talc, gypsum, and chalk, may be used partially to replace clay as paper fillers. Several substitutes have been found to replace fuller's earth and bentonite as oil clarifiers. In many nonceramic uses, clays are used because they are less expensive than other materials having equal or better qualifications.

Bauxite replaces fire clay in refractory uses and activated bauxite competes with activated bentonite and fuller's earth in mineral oil bleaching and filtration. Cinders, blast-furnace slag, pumice, and perlite are substitutes for expanded clay and shale lightweight aggregate in some uses. Argillaceous limestone (cement rock), where available, reduces or eliminates the need for clay in manufacturing cement.

RESERVES

Clay resources in the United States are sufficient to supply essentially all requirements for the next century with exception of fire clay.

Miscellaneous clays and shales suitable for production of clay construction products and cement occur in all States. Many of the deposits contain material suitable for production of lightweight aggregates, and a systematic study is under way to locate suitable clays and shales for this purpose (*11*, *14*, *17*, *19*, *29*, *31*, *45*).

Bentonite deposits in Wyoming, Montana, and South Dakota contain several hundred million tons of minable reserves (*25*, *26*). Deposits also occur in Mississippi, Texas, and other States.

There are large deposits of attapulgite fuller's earth in Florida and Georgia. Montmorillonite fuller's earth occurs in large quantities in Mississippi and western Tennessee and Kentucky. Other deposits of fuller's earth are in Utah, Texas, California, and Nevada. Quantitative ore reserve data are not available.

The largest domestic ball clay deposits are in Tennessee, Kentucky, and Mississippi. Other deposits are in California and Maryland.

Kaolinitic clays are widespread in the central and eastern States, and most deposits are of ceramic-grade material. High-grade kaolin deposits containing paper coating and filler quality materials are mostly in Georgia and South Carolina with smaller deposits in Alabama, California, Connecticut, Florida, and other States.

Fire clay resources are found in most areas of the United States, and deposits in about 30 States have been exploited in recent years. Although the overall reserves are large, the super duty and high-heat duty clays in some areas are becoming exhausted. The Missouri fire clay districts are a notable example, and re-

search is being conducted toward removal of detrimental impurities from material representing large deposits of presently submarginal but potentially high-grade fire clays (*8*, *38*, *39*).

CONSERVATION

Because of the relatively large supply of clays, little effort has been directed toward conservation. However, there is substantial interest in the possibility of expanding the supply of high-grade refractory and paper clays by beneficiating inferior clays, which would extend the productive life of the existing high-grade kaolin and refractory-grade clay deposits. The Bureau has recently conducted research to this end with encouraging results.

SOURCES OF STATISTICAL INFORMATION

Clays-production statistics are obtained and tabulated by the Bureau of Mines from all known producers. The Bureau of the Census compiles and publishes monthly statistics of the quantity and value of shipments of the principal structural clay products in the United States and quarterly reports on the production and shipments of clay and nonclay refractories, by type (*47*, *48*). The Department of Commerce also compiles data on imports of various types of clay. Data on exports from the United States are obtained by the Bureau of the Census and from producers canvassed by the Bureau of Mines. Data on production and import-export trade in foreign countries are obtained from various sources, including mineral industry reports gathered by the Department of State. These data are adequate for most U.S. Government and industry purposes. Canadian Government statistics are exceptionally complete and reliable and provide a sound basis for evaluating the interrelationships between the United States and Canadian clay industries.

PRODUCTION, CONSUMPTION, AND TRADE

Detailed data on kinds of clay sold and used, and the quantities going for major uses are shown in table 2. The production of clays of various kinds was reported from 48 States, and the District of Columbia in 1963 (see table 3). Alaska and Rhode Island were the only States not reporting. Miscellaneous clay was recovered in all reporting States, and fire clay in 29 States. About 60 percent of the total clays sold or used was reported from 10 States—Ohio, Georgia, Texas, California, Pennsylvania, North Carolina, Michigan, Illinois, Missouri, and Alabama. The same 10 States accounted for 63 percent of the clay value. Consumption of clays for 1949–63 is given in table 4.

Nonceramic uses accounted for 43 percent of all clays consumed in 1963, compared with 38 percent in 1959 and 32 percent in 1954. The major factor causing the increase in nonceramic use was the production of expanded clay and shale aggregates which required 13.5 percent of total clays consumed in 1963 compared with 3.6 percent in 1954. With minor exceptions the percentages required for other nonceramic uses have remained constant during the past decade.

U.S. imports of clays have not been a significant factor in the industry in recent years. Before World War I, most of the kaolin and ball clays used in the United States were imported, principally from England, but domestic material now dominates the market for all types of clay, except in areas where the freight differentials favor imports and where consumers prefer the imported clays. Small quantities of all types of clays, except miscellaneous clay, are imported from the United Kingdom, West Germany, Canada, and other countries. Total imports of clays into the United States in 1963 were 126,000 tons, valued at $2.4 million. Beginning in 1954 separate data have been available only for kaolin and common blue and ball clays.

Exports from the United States include kaolin and fire clay for which separate data are available. Bentonite and fuller's earth probably comprise the greater part of the balance of clay exports but they are not reported separately. In 1963, total clay exports were 739,000 tons valued at $21 million, representing less than 2 percent of the total U.S. production, but nearly 12 percent of the value.

Under paragraph 207, schedule 2, of the Tariff Act of 1930, clay or kaolin, bentonite, fuller's earth, and clays or earths artificially activated are dutiable. In addition, some other kinds of clays are dutiable under the category of "clays or earths, including common blue clay and Gross Almerode glass-pot clay, n.s.p.f. (not specifically provided for)." The clays in the latter category include low-grade building-brick clays, high-grade ball clays, stoneware clays, and fire clays. In the latest tariff schedules ball clays have been separated from this blanket category. The history of tariffs on the dutiable classes of clays is given in table 5.

TABLE 2.—*Clays sold or used by producers in the United States in 1963 by kinds and uses*

[Short tons]

Use	Kaolin	Ball clay	Fire clay and stoneware clay	Bentonite	Fuller's earth	Miscellaneous clay including slip clay	Total
Pottery and stoneware:							
Whiteware, etc.	[1] 129,780	[1] 273,588					[1] 403,368
Stoneware, art pottery, flowerpots, and glaze slip	[1]	[1]	44,798			63,000	[1] 107,798
Total	129,780	273,588	44,798			63,000	511,166
Floor and wall tile	5,556	119,492	231,492			77,953	434,493
Refractories:							
Fire brick and block	235,789	19,440	2,844,230			17,277	3,116,736
Bauxite, high-alumina brick	[2]		44,054			253,258	[3] 297,312
Fire-clay mortar			83,101			[2]	[3] 83,101
Clay crucibles			[2]			[2]	[2]
Glass refractories	[2]	[2]					[2]
Zinc retorts and condensers			[2]				[2]
Foundries and steelworks	[2]	[2]	602,211	[4] 466,614		[2]	1,082,893
Saggers, pins, stilts, and wads	[2]	[2]	[2]				72,443
Other refractories	60,074	65,809	244,183	[4]		14,233	297,788
Total	295,863	85,249	3,817,779	466,614		284,768	4,950,273
Heavy clay products: Building brick, paving brick, drainage tile, sewer pipe, and kindred products		[5]	4,180,310			18,403,162	[5] 22,583,472
Architectural terra cotta	3,420		4,095				7,515
Lightweight aggregates						6,796,961	6,796,961
Filler:							
Paper filling	601,062						601,062
Paper coating	1,046,091						1,046,091
Rubber	443,417		[2]				[3] 443,417
Paint	62,344		[2]				[3] 62,344
Fertilizers	12,121		[2]			[2]	[3] 12,121
Insecticides and fungicides	33,579		4,914	7,263	95,382	[2]	[3] 141,138
Other fillers	111,601	[5]	5,224	940	[5]	[5]	129,432
Total	2,310,215	[5]	10,138	8,203	[6] 95,382	[5]	2,435,605
Portland and other hydraulic cements	[5]			[5]		10,204,146	10,313,065
Miscellaneous:							
Filtering, decolorizing, and clarifying				68,186	41,839		110,025
Rotary-drilling mud			[5]	432,493	62,371	7,329	[6] 502,193
Chemicals	[5]		[5]	[5]	[5]		118,508
Absorbent uses	[5]		[5]	[5]	248,293	[5]	388,405
Exports	156,892	[5]		[5]	[5]	[5]	243,574
Enameling	[5]	[5]		[5]			[5]
Catalysts (oil refining)	[5]						[5]
Pelletizing:							
Iron ore				278,849			278,849
Other				14,318	[5]		[6] 14,318
Other uses	261,847	69,339	101,562	315,853	33,932	193,935	510,580
Total	418,739	69,339	101,562	1,109,699	386,435	201,264	2,166,452
Grand total:							
1963	3,163,573	547,668	8,390,174	1,584,516	481,817	36,031,254	50,199,002
1962	2,998,157	486,936	8,065,048	1,444,135	409,989	34,392,061	47,796,326

[1] Some stoneware, art pottery, etc., included with whiteware.
[2] Included with "Other."
[3] Incomplete figure; remainder included with "Other."
[4] Some "Other refractories" included with foundries.
[5] Included with miscellaneous "Other uses."
[6] Incomplete figure; remainder included with miscellaneous "Other uses."

STRATEGIC CONSIDERATIONS

The United States is self-sufficient in clays, although cost and consumer preferences provide a relatively small market for a few types of imported clays. As the Missouri diaspore and burley clays are exhausted some consumers are placing increasing reliance on bauxite from Caribbean sources for use in manufacturing high-alumina refractories. Bauxite clays from the Caribbean area also could be utilized extensively in future production of lower duty refractories.

No defense programs have been required for clays, although a strategic stockpile of refractory-grade bauxite has been established to provide material for high-alumina refractories if shipments from British Guiana and Surinam should be interrupted in wartime.

TABLE 3.—*Clays sold or used in the United States in 1963, by States, and by kinds*

[Thousand short tons]

State	Kaolin	Ball clay	Fire clay	Bentonite	Fuller's earth	Miscellaneous clay	Total
Alabama	(1)	------	221	------	------	1,387	[3] 1,607
Arizona	------	------	(2)	(1)	------	162	[3] 163
Arkansas	------	------	194	------	------	574	769
California	19	(1)	531	21	(1)	2,801	3,395
Colorado	------	------	194	1	------	491	686
Connecticut	------	------	------	------	------	189	189
Delaware	------	------	------	------	------	13	13
District of Columbia	------	------	------	------	------	78	78
Florida	(1)	------	------	------	(1)	(1)	538
Georgia	2,490	------	------	------	137	1,581	4,208
Hawaii	------	------	------	------	------	(2)	------
Idaho	(1)	------	(1)	(2)	------	31	[3] 31
Illinois	------	------	332	------	------	1,617	1,949
Indiana	------	------	448	------	------	1,098	1,546
Iowa	------	------	31	------	------	1,033	1,064
Kansas	------	------	(1)	------	------	(1)	893
Kentucky	------	(1)	211	------	------	772	[3] 984
Louisiana	------	------	------	------	------	655	655
Maine	------	------	(2)	------	------	42	42
Maryland	------	(1)	(1)	------	------	552	580
Massachusetts	------	------	------	------	------	157	157
Michigan	------	------	------	------	------	1,958	1,958
Minnesota	------	------	(1)	------	------	199	[3] 199
Mississippi	------	(1)	157	280	(1)	725	1,235
Missouri	------	------	850	------	------	897	1,746
Montana	------	------	(1)	------	------	38	[3] 38
Nebraska	------	------	------	------	------	148	148
Nevada	------	------	(2)	(2)	(1)	(1)	------
New Hampshire	------	------	------	------	------	110	110
New Jersey	------	------	107	------	------	391	498
New Mexico	------	------	(1)	------	------	(1)	------
New York	------	------	------	------	------	1,598	1,598
North Carolina	(1)	------	------	------	------	2,735	[3] 2,735
North Dakota	------	------	5	(2)	------	(1)	[3] 5
Ohio	------	------	2,253	------	------	2,588	4,841
Oklahoma	------	------	(2)	(1)	------	897	[3] 898
Oregon	------	------	------	(1)	------	(1)	279
Pennsylvania	(1)	------	1,505	------	------	1,686	[3] 3,191
South Carolina	485	------	------	------	------	1,006	1,491
South Dakota	------	------	------	(1)	------	(1)	315
Tennessee	------	355	------	------	(1)	882	[3] 1,238
Texas	------	------	808	120	(1)	3,271	[3] 4,199
Utah	(1)	------	(1)	7	3	115	[3] 125
Vermont	(1)	------	------	------	------	(1)	------
Virginia	------	------	------	------	------	1,410	1,410
Washington	------	------	(1)	(2)	------	134	[3] 134
West Virginia	------	------	237	------	------	178	414
Wisconsin	------	------	------	------	------	111	111
Wyoming	------	------	(1)	991	------	(1)	1,113
Undistributed	167	192	306	164	341	1,721	623
Total	3,163	547	8,390	1,584	481	36,031	50,199

[1] Included with undistributed to avoid disclosing individual company confidential data.
[2] Less than 500 tons.
[3] Incomplete total because of concealed data for some types of clay.

PRICES AND COSTS

Prices quoted in Oil, Paint and Drug Reporter for December 1963 for various clays were as follows:

Bentonite:
200-mesh, bags, carlots, f.o.b. mines, per short ton, $14.

Fuller's earth (February 1960):
Insecticide grade, dried, powdered, bags, carlots, Georgia or Florida mines, per short ton, $17.50.
Oil-bleaching grade, 100-mesh, bags, carlots, per short ton, $16.30–$17; 200-mesh, bags, carlots, per short ton, $17.50–$18.

Ball clay:
Domestic, air-floated, bags, carlots, Tennessee, per short ton, $18–22; crushed, shed moisture, bulk, carlots, Tennessee, per short ton, $8–$11.25.
Imported, air-floated, bags, carlots, Atlantic ports, per ton, $43–$47; lump, bulk, carlots, Atlantic ports, per ton, $31.50–$37.50.

China clay:
Domestic, dry-ground, calcined, air-floated, bags, carlots, f.o.b. plant, Georgia, per short ton, $43–$68; dry ground, air-floated, 99 percent 325-mesh, bags, carlots, f.o.b. plant, Georgia, per short ton, $11–$17; water-ground, washed, bags, carlots, f.o.b. plant, per short ton, $21.50–$50.
Imported, white, lump, bulk, carlots, ex dock, Philadelphia, Pa., and Portland, Maine, per long ton, $23–$35; powdered, bags, carlots, ex dock, per short ton, $50.

The quoted prices indicate only the range of prices. Actual prices are subject to individual negotiation between buyers and sellers, and depend on the degree of processing, type of packaging, and many other factors. Prices for fire clay and miscellaneous clay, a large proportion of which is produced in captive operations, are not quoted in trade journals.

Changing practices in past reporting of unit values make it almost impossible to arrive at reliable long-term comparisons. However, prices have remained fairly constant for relatively long periods.

TABLE 4.—*Clays sold or used by producers in the United States for ceramic and nonceramic uses*

[Thousand short tons]

Uses	1954	1955	1956	1957	1958	1959	1960	1961	1962	1963
Ceramic:										
Pottery and stoneware	423	528	571	420	412	496	509	461	514	511
Floor and wall tile	304	346	306	402	412	430	394	318	362	435
Refractories	4,733	6,315	6,868	6,386	4,528	6,189	6,351	5,081	4,835	4,950
Heavy clay products	23,416	25,508	26,109	22,266	21,535	23,353	23,383	21,908	21,547	22,591
Total	28,876	32,697	33,854	29,474	26,887	30,468	30,637	27,768	27,258	28,487
Percent	68.0	68.0	66.4	64.4	61.4	61.7	62.4	58.6	57.0	56.8
Nonceramic:										
Portland and other hydraulic cements	8,779	9,055	9,291	8,994	9,107	10,073	9,301	9,762	9,585	10,313
Lightweight aggregate	1,549	3,094	4,144	3,753	4,465	5,270	5,504	6,047	6,770	6,797
Filler	1,326	1,460	1,814	1,753	1,787	2,031	2,105	2,162	2,322	2,436
Miscellaneous	2,102	1,936	1,871	1,736	1,504	1,541	1,522	1,652	1,861	2,166
Total	13,756	15,545	17,120	16,236	16,863	18,915	18,432	19,623	20,538	21,712
Percent	32.0	32.0	33.6	35.6	38.6	38.3	37.6	41.4	43.0	43.2
Grand total	42,632	48,242	50,974	45,710	43,750	49,383	49,069	47,391	47,796	50,199
Percent	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

TABLE 5.—*U.S. import duties on clays*

	Act 1930–33	Effective Jan. 1, 1939	Effective Jan. 1, 1948	Effective June 30, 1956	Effective June 30, 1957	Effective June 30, 1958	Effective Aug. 31, 1963
	Rates per long ton						
China clay or kaolin	$2.50	$1.75	$1.25	$1.18	$1.12	$1.06	0.67
Common blue clay and other ball clays:							
Unwrought and unmanufactured	1.00	1.00	1.00	.95	.90	.85	[1] .62
Wrought or manufactured	2.00	2.00	2.00	1.90	1.80	1.70	[1] 1.21
Bentonite:							
Unwrought and unmanufactured	1.50	.75	.75	.375	.375	.375	(.8125)
Wrought or manufactured	3.25	1.62½	1.62½	.8125	.8125	.8125	
Fuller's earth:							
Unwrought and unmanufactured	1.50	1.00	.50	.50	.50	.50	.50
Wrought or manufactured	3.25	2.00	1.00	1.00	1.00	1.00	1.00
Clays or earths, n.s.p.f.:							
Unwrought and unmanufactured	1.00	1.00	1.00	.95	.90	.85	.50
Wrought or manufactured	2.00	2.00	2.00	1.90	1.80	1.70	1.00
	Rates per pound						
Clays or earths, artificially activated with acid or other material:							
Cents per pound	¼¢	¼¢	¼¢	0.11¢	0.11¢	0.10¢	0.10¢
Percent ad valorem	plus 30	plus 30	plus 30	plus 14	plus 13½	plus 12½	plus 12½

[1] Effective Jan. 1, 1964.

TAXES

No special taxes are imposed on the clay industry. Producers of kaolin, ball clay, bentonite, fuller's earth, and fire clay are granted a depletion allowance of 15 percent on both domestic and foreign production. Producers of brick and tile clay are granted an allowance of 5 percent for foreign and domestic production.

TRANSPORTATION

Transportation is a relatively small factor in the clay-processing industries. Most of the miscellaneous-clay and fire-clay processing plants, which use about 90 percent of the clay consumed annually, obtain their supply of raw material from deposits adjacent to the plant. Only the relatively high-grade ball clays, kaolin, bentonite, and fuller's earth are transported long distances to consuming centers.

Transportation is a major factor in marketing of brick, tile, lightweight aggregates and other clay construction products. Only in special cases can the marketing radius exceed a few hundred miles.

RESEARCH

Research on clays is presently being conducted by a large number of public and private organizations and for a diversity of purposes. Geologic correlations are frequently made on the basis of the types and quantities of clay minerals present, and much work on this subject is conducted by Federal and State geological surveys, and by universities. Much work is done by the Federal Bureau of Mines, National Bureau of Standards, and by private industry on improvement of clays for ceramic and other purposes by beneficiation for removal of impurities, and on modification or improvement of clay minerals by heat treatment and by reaction with organic and inorganic chemicals. New methods for identification and study of clay minerals are being developed, and the structure of clay minerals is receiving a large share of attention by researchers.

During World War II the Bureau of Mines did exploratory work to find high-alumina clays and conducted extensive pilot-plant research and investigation to produce alumina suitable for manufacturing aluminum from clays. Several different processes were tried. The Bureau of Mines is presently evaluating a number of alumina-from-clay processes developed by Government and industry to determine which has the most merit.

During the past decade the Bureau has conducted research on beneficiation of refractory and paper clays and the evaluation of clays and shales for thermally expanded lightweight aggregate and other uses. Surveys were completed by the Bureau on refractory clay deposits in a number of western States and on expandable clays and shales in many of the North Central States. Similar studies were under way in other areas. Technologic and economic studies are coordinated to assist industry in assuring adequate supplies of clays at minimum cost to meet national, regional, and local requirements.

OUTLOOK

Production of clays in general should continue to climb approximately in proportion to the GNP but at a slightly slower rate. Many of the individual types of clays are subject to fluctuations from factors which bear no direct relationship to the GNP.

Bentonite production in Wyoming is in a period of rapid expansion due to conversion of iron ore processing facilities in the United States and Canada for production of high-grade iron ore pellets using bentonite as a binder. Legislation providing for an equitable taxation arrangement between the State government and the iron ore producers in the Minnesota taconite areas was passed in 1964, and this should further accelerate bentonite production for pelletizing.

Production of clay and shale for lightweight aggregates will probably continue to increase at a rate somewhat above that of the GNP but not as rapidly as it has during the past 10 years. As indicated by recent practice, new plants will be larger and more efficient.

Use of fire-clay refractories should continue to decrease for several years due to many factors. Increased labor costs have made it necessary for many refractories users to switch to more expensive refractories with long service life to minimize maintenance and replacement costs. The rapid conversion of steel plants to the basic-oxygen processes has reduced the requirements for fire-clay refractories. Furthermore, the operating temperatures now prevalent in many nonferrous metallurgical plants are higher than the rated limits of fire clays. Exhaustion of fire-clay reserves in some areas of the United States has accelerated the use of other refractories.

The consumption pattern for fuller's earth is changeable and will probably continue to be so. However, due to its versatility the demand for fuller's earth is expected to continue to increase at a rate somewhat higher than that of clays in general. Absorbent uses which are growing rapidly, should account for over half of the production during the next 5 years. Use of fuller's earth as a soil conditioner on golf courses and sports arenas is also expected to increase rapidly.

Paper coating and filler will continue to account for the greater part of kaolin produced in the United States, with other fillers, refractories, high-quality ceramics, and chemicals taking the balance. An annual growth rate of 5 to 6 percent is indicated.

Ball-clay production should increase 3 to 4 percent per year for the next 5 years.

Output of clays and shales for brick, tile, and other clay construction products should remain fairly constant, with possible slight increases over the next 10 years due to the improving competitive position of the structural clay-products industry.

PROBLEMS

Perhaps the most important problem confronting the clay industry is in structural clay products, where the intense competition from other construction materials is threatening, and in some cases replacing, clay brick and tile. The principal competing products are glass, metals, and conventional and special concretes.

Fire clay and fire-clay refractories industries are threatened from several directions. In some local areas the high-grade fire-clay deposits are becoming exhausted. Competition from other refractories is increasing because of technologic changes and because of the higher maintenance and replacement costs involved with the fire-clay products. In local areas where common clays are not readily available or where there is no current demand for fire clay for refractories production, fire-clay deposits are being depleted by use of this material in clay construction products.

Bentonite is being used in increasing quantities for pelletizing iron ore concentrates, and new mining and processing facilities are being built in Wyoming to provide the material. However, the transportation cost to some pelletizing plants exceeds the basic cost of the bentonite, and new, lower cost binders are being sought, which could adversely affect the growth of the bentonite producing industry.

Much low-grade kaolin is produced along with material of paper coating quality in the South Central States. Improvement of the low-grade material by fine grinding is technically feasible, but economic large-scale processing facilities have not yet been developed. Until this problem is solved much potentially valuable material will be wasted or sold for low quality filler and ceramic uses.

Data are lacking in many States on the quantities and qualities of clay and shale suitable for production of expanded lightweight aggregates. Lack of adequate data on potential markets for lightweight clay and shale aggregate in some areas also prevents the optimum growth of the lightweight aggregate industry.

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COBALT

By Glen C. Ware [1]

THE history of cobalt dates to ancient times. Its earliest use was solely as a coloring agent which imparted the brilliant blue hue to early ceramics and glass. The Chinese developed the art of cobalt coloring to a high degree during the Ming Dynasty. In Europe the Venetian artisans of the 15th century were using various cobalt compounds to color their renowned glassware.

Chief minerals of cobalt are in four major categories—arsenides, sulfides, sulfarsenides, and oxidized minerals. Large deposits occur in Canada, Cuba, Morocco, Northern Rhodesia, and the Republic of the Congo from which cobalt is extracted as a coproduct or byproduct of copper or nickel. The extraction of cobalt from ores and concentrates requires complex and complicated operations in mineral dressing, pyrometallurgy, hydrometallurgy, and electrochemistry.

The United States, the largest consumer of cobalt, used an average of 10 million pounds per year during 1959–63. Industrial consumption in 1963 was 10.5 million pounds. The largest single use of cobalt, 23 percent of the 1963 total, was for high-temperature, high-strength alloys. The use for permanent magnet alloys was second with 22 percent of the total cobalt consumed. Uses in steel amounted to 12 percent of the total.

Bethlehem Cornwall Corp. is the only domestic producer of cobalt concentrate. Pyrites Co., Inc., Wilmington, Del., processes the concentrate into metal, oxide, and hydrate.

Free world production of cobalt in 1963 was 12,700 tons, of which the Republic of the Congo produced 63 percent, and Morocco and Canada produced 12 and 11 percent, respectively. Production exceeds free world demand, but there is substantial demand for the commodity in Communist countries.

The principal problem facing major producers is the disposal of surplus cobalt inventories. Another problem of considerable importance is the high cost of the metal, attributed primarily to the involved and costly processes required and to low yields. The price of $1.50 per pound restricts its use and favors the employment of less expensive substitutes, notably nickel. Among the technological problems are lack of full understanding of the properties of cobalt metal and its role in various alloys, lack of more efficient processing methods and equipment to lower the cost of production, and a great need for more and better manufacturing techniques to expand outlets for cobalt.

BACKGROUND

Cobalt's chemistry and metallurgy date to the middle 16th century when silver-cobalt ores were mined in the Harz Mountains of Germany. These ores contained arsenic which formed poisonous fumes during roasting. The arsenic also caused ulceration of the hands and feet of the miners. They associated their sufferings with gnomes and goblins called Kobolds, and probably the name "cobalt" was derived from this term.

The development of the cobalt industry in Germany is obscure. According to the best accounts, Weidenhammer, in 1520 at Schneeberg, Saxony, was the first to set up a mill; the mill made blue color, known as safflor or saffre. This was a crude cobalt oxide made by crushing and roasting the ore.

Other European countries mined cobalt in later years, but the supply was limited. This small European supply was greatly augmented upon the discovery of large deposits in New Caledonia by Garnier in 1864. These deposits remained the chief cobalt source until about 1903 when the rich silver-cobalt ores of Ontario, Canada, were discovered. Little interest was shown in the Canadian ore until silver was

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found in the ore. Consequently, output, as a byproduct of silver refining, increased from 16 tons in 1904 to 1,553 tons in the next 5 years. As Canadian competition increased, the cobalt industry in New Caledonia went into a spiraling decline and ceased cobalt production altogether by 1911.

Mining of cobalt-bearing copper ores began in Katanga Province in the former Belgian Congo about 1910 by Union Minière du Haut-Katanga. About 1920, the firm started to extract cobalt from the ores, and by 1926 it had become the world's leading producer—a position it still retains by a wide margin. Since then, cobalt deposits have been discovered and developed in other parts of Africa, notably Northern Rhodesia and Morocco.

During the late 1800's and early 1900's there were efforts to start a domestic cobalt industry. In 1869 cobalt oxide was produced, probably from raw materials of Canadian origin. For the most part, operations were exceedingly small and did not last long. Consumption of cobalt did not increase substantially until the 1940's, when military needs developed. Then, in fear of being severed from foreign sources, efforts were intensified to develop domestic sources. The Pyrites Co., Inc., Wilmington, Del., started production of cobalt oxide from concentrate, which was supplied by the Bethlehem Cornwall Corp. In 1944, St. Louis Smelting & Refining Co. began commercial production of cobalt from its Fredericktown, Mo., property. Spurred by the war effort, other firms started cobalt production.

After the war, interest in cobalt waned. Consequently, many of the wartime facilities were forced to close. Interest was revived by the Korean conflict. The Calera Mining Co. started and then expanded its production plants in the Blackbird district in Lehmi County, Idaho, at the request of the Federal Government. In return for the expansion the Government in 1951 contracted with the company to purchase initially 6.5 million pounds of cobalt at a fixed premium price. St. Louis Smelting & Refining Co. reopened its cobalt producing facilities in 1955. In 1958, the domestic cobalt industry reached its peak production with 4 million pounds of recoverable cobalt. In 1959, production fell sharply on account of foreign competition and curtailed demand by the Government. Unable to meet foreign competition, Calera Mining Co. closed in mid-1959 after making final deliveries to the Government. St. Louis Smelting & Refining Co. closed in early 1961.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Most of the world's cobalt is recovered as a minor byproduct of copper or nickel refining. Bethlehem Cornwall Corp. in Pennsylvania is now the sole domestic supplier. Approximately 21 domestic firms, the 3 largest in Cleveland and Cincinnati, Ohio, and Elizabeth, N.J., annually make various products containing about 1 million pounds of cobalt starting with purchased cobalt hydrate, sulfate, scrap, and virgin metal. Chief products are cobalt salts, driers, and related compounds. A list of the companies and their respective products is given in table 1.

World cobalt production is centered in the Republic of the Congo. Union Minière du Haut-Katanga, the sole cobalt producer in the Congo, has mines and concentrating plants near Jadotville and Kolwezi. Its refineries are situated at Jadotville and Luilu. The company also maintains cobalt refining facilities at Oolen, Belgium. Sales of the firm's products in the United States are handled by African Metals Corp., New York, N.Y., and Chicago, Ill.

In Northern Rhodesia cobalt is produced as a byproduct of copper processing by Rhokana Corp. at its electrolytic refinery near Nkana, and by Chibuluma Mines, Ltd., near Ndola. The latter firm produces a matte, which is shipped to Belgium for further refining.

In Canada, cobalt is produced chiefly as a byproduct or coproduct from nickel-copper ores in the Sudbury district, Ontario, and the Lynn Lake area, Manitoba. Some small outputs resulting from precious metal refining still come from the silver-cobalt ores in the Cobalt, Gowganda, and Timiskaming areas. Cobalt-nickel ore is refined at Port Colborne, Ontario, by International Nickel Co. of Canada, Ltd.; at Kristiansand, Norway, by Falconbridge Nickel Mines, Ltd.; and at Fort Saskatchewan, Alberta, by Sherritt Gordon Mines, Ltd. The facilities of the Deloro Smelting & Refining Co., Deloro, Ontario, an appreciable cobalt producer at one time, were closed in March 1961.

In Finland, cobalt is produced from the cupriferous pyrite of the Outokumpu mine of Outokumpu Oy in the eastern part of the country. Sinter produced by roasting pyrite concentrate to remove the sulfur is shipped to Duisburger Kupferhütte at Duisburg, West Germany, for recovery of cobalt.

TABLE 1.—*Refiners or processors of cobalt in the United States in 1963*

Refiner or processor	Location of plant	Cobalt product made [1]	Cobalt raw material used [1]
Allied Chemical Corp., General Chemical Division	Marcus Hook, Pa.	B, D	A
Baker Chemical Co., J. T.	Phillipsburg, N.J.	B, D	A
Carlisle Chemical Works, Inc., Advance Solvents and Chemical Division	New Brunswick, N.J.	E	A, D
Ceramic Color & Chemical Manufacturing Co.	New Brighton, Pa.	C, D	A
Chase Chemical Corp.	Pittsburgh, Pa.	E	C
Ferro Chemical Corp.	Bedford, Ohio	C, D, E	A, C
Hall Chemical Co.	Wickliffe, Ohio	B, C, D	A, G
Harshaw Chemical Co.	Cleveland, Ohio; Gloucester, N.J.	C, D, E	A
Mallinckrodt Chemical Works	St. Louis, Mo.	D	A, D
McGean Chemical Co.	Cleveland, Ohio	C, D, E	A
Mooney Chemicals, Inc.	do.	E	A
Nuodex Products Co., Inc.	Elizabeth, N.J.; Long Beach, Calif.	E	
Peck Hydrometallurgical Co.	Portsmouth, Va.	B, D	G
Pyrites Co., The	Wilmington, Del.	A, B, C	F
Shepherd Chemical Co.	Cincinnati, Ohio	D, E	A, C, D, G
Sherwin-Williams Co.	Chicago, Ill.	E	A, C
Standard Oil Co. of California	Richmond, Calif.	E	A
Stresen-Reuter, Inc., Frederick A.	Bensenville, Ill.	C, D, E	A, C
Troy Chemical Co.	Newark, N.J.	E	A
Whitmoyer Laboratories, Inc.	Myerstown, Pa.	D	A, C
Witco Chemical Co.	Chicago, Ill.	C, E	A

[1] Code: A, metal; B, oxide; C, hydrate; D, salts; E, driers; F, concentrate; G, scrap.

Cobalt production in Morocco is by La Société Minière de Bou-Azzer et du Graara, which operates a mine and a concentrator south of the Atlas Mountains near Bou-Azzer. The concentrate is shipped to France and Belgium for further processing.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Cobalt is a silvery-gray metal with a slight bluish tinge, closely resembling nickel in appearance and in many of its properties. It is, however, somewhat harder and more brittle than nickel. Its occurrence is widely distributed and is usually found associated with other metals.

Most of the cobalt used by industry is in the form of metal. Other cobalt forms commonly used are oxides and the salts. Cobalt metal is produced as briquets, granules, squares, broken cathodes, rondelles, fines, and powder. Squares are made by cutting cathodes into square pieces of 1, 2, or 4 inches on a side. Broken cathodes are produced by feeding cathodes through toothed rolls. Rondelles are made by converting compacted pellets of cobalt oxide to metal. Fines are relatively impure form of cobalt produced as an intermediate product in the refining circuit. Cobalt powder is generally made by reducing cobalt oxides with hydrogen and by mechanical grinding of rondelles and other cobalt metal forms. Table 2 gives typical analyses of cobalt metal from leading suppliers.

Cobalt forms three stable oxides—cobaltous oxide (CoO), cobaltic oxide (Co_2O_3), and cobaltosic oxide (Co_3O_4). Only the gray oxide, consisting mainly of cobaltous oxide, and the black oxide, consisting mainly of cobaltosic oxide, are used commercially to any appreciable amount.

The primary producers of salts and related compounds market six cobalt salts—cobalt acetate, carbonate, chloride, nitrate, and sulfate. Many other cobalt salts and compounds are manufactured by producers from cobalt scrap or from one of the aforementioned salts. Nearly all of the cobalt salts used for commercial purposes are in the cobaltous state.

TABLE 2.—*Nominal analyses of commercial cobalt metal*

[Percent]

Supplier and forms	Cobalt	Nickel	Iron	Copper	Sulfur	Carbon
Falconbridge Nickel Mines, Ltd.: Broken cathodes	99.60	0.33	0.003	0.004	0.002	0.015
International Nickel Co.: Electrolytic squares	99.5+	.45	.005	.005	.001	0.01–0.02
Sherritt Gordon Mines, Ltd.:						
Briquets	99.8	.10	.01	.005	.005	.01
Powder	99.8	.10	.01	.005	.03	.05
Union Minière du Haut-Katanga:						
Granules	99.60	.18	.10	.01	.01	.01
Rondelles	99.25	.30	.04	.001	.006	.007
Powder (100-, 300-, and 400-mesh)	99.50	.08	.09	.001	.015	.030
Powder (400-mesh low C)	99.60	.08	.09	.001	.010	.015
Powder (extra fine)	99.68	.012	.015	.001	.005	.030

TECHNOLOGY

Geology

Cobalt is about as abundant as lead in the earth's crust. The average content is estimated to be 23 parts per million. Unlike lead, however, it is widely diffused in nature and does not occur in heavy concentrations. For the most part cobalt is associated with ores of copper, nickel, iron, silver, manganese, lead, and zinc.

The three important types of cobalt minerals are sulfides, arsenides, and oxides. The principle sulfide minerals are carrollite (Co_2CuS_4) and linnaeite (Co_3S_4). The principle arsenide minerals are smaltite ($(CoNi)As_2$, safflorite ($(CoFe)As_2$, skutterudite ($(CoNi)As_3$, and cobaltite (CoAsS). The principle oxide minerals are asbolite ($CoO \cdot 2MnO_2 \cdot 4H_2O$), heterogenite ($CoO \cdot 2Co_2O_3 \cdot 6H_2O$), sphaerocobaltite ($CoCO_3$), and erythrite ($3CoO \cdot As_2O_5 \cdot 8H_2O$). Seldom are any of the cobalt minerals found in sufficient quantity to be mined for cobalt alone. Consequently, the amount and concentration of cobalt and the presence of associated metals are factors in making deposits of economic value.

Magmatic differentiation, which produces basic and ultrabasic rocks, seems to concentrate cobalt along with nickel, chromium, and some other metals. The ultrabasic rocks, such as serpentine, do not contain cobalt in commercial quantities. The soil formed from them, however, has concentrations of iron, manganese, nickel, and cobalt after long successive weathering of the rocks, especially under tropical conditions that cause much laterization. The best known examples of such cobalt deposits are the lateritic iron ores. The basic rocks are generally associated with concentrations of iron nickel, and copper sulfides. Most geologists believe that some hydrothermal activity as well as magmatic differentiation is important in the origin of these cobalt deposits. Where the deposits are large, such as at Sudbury, Ontario, some cobalt can be recovered as a byproduct during the recovery of nickel and copper.

Hydrothermal activity has formed by far the largest number of cobalt deposits. Some of the deposits contain sufficient cobalt to be minable as originally formed. Others have been enriched by weathering. There are several types of hydrothermal activity, simplest hydrothermal deposits being veins containing cobaltite in a quartz or calcite gangue. A few such simple veins of cobalt ore have been worked in the Cloncurry district of Australia. For the most part, however, cobalt deposited in this manner is found in relatively small quantities associated primarily with copper deposits. The copper-cobalt ores in the Katanga-Northern Rhodesia districts are examples of such deposits.

Mining

Most cobalt is recoved as a byproduct or coproduct in treating ores of copper and nickel, and descriptions of mining practices as applied to these ores are presented in their respective commodity statements.

Metallurgy

Owing to the variations in cobalt content and type of mineralization of copper-cobalt ores, Union Minière refines cobalt by several distinct methods. Milling and concentrating procedures also depend upon the nature of the ores. The following types of ore are treated separately at the Kolwezi concentrator; copper oxide ore containing small amounts of cobalt, cobalt-copper oxide ore containing approximately equal amounts of the two metals, and mixed ore containing both the oxides and sulfides of copper and cobalt. The copper oxide concentrate is sintered and smelted in an electric-arc furnace at the Panda plant in Jadotville. The four electric furnaces there have a combined annual capacity of 4,400 tons of contained cobalt (*18*).[2] The charges to the electric furnaces are fluxed and reduced by a lime and coal mixture.

The resulting melt is drawn into ladles where it separates into two molten alloys of different density. The bottom layer of so-called red alloy has a composition of 89 percent copper and 4.5 percent cobalt. The top layer, called white alloy, contains approximately 42 percent cobalt, 15 percent copper, and 34 percent iron. The red alloy is later refined to copper at the Panda smelter. During refining, cobalt is slagged off and returned to the electric furnaces. The white alloy is cast into ingots and shipped to the Oolen plant of the Société Générale Metallurgie de Hoboken in Belgium for further processing.

The second type of product, cobalt-copper oxide, from the Kolwezi concentrator is processed in Union Minière's Jadotville-Shituru hydrometallurgical plants. Sulfuric acid is used to leach the metal out of the concentrates. The leached products are then subjected to a series of processes that include: classification to remove the sand, decantation, countercurrent washing, and careful clarification to remove suspended particles. Clarification is accomplished by filtering the solution through finely

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

divided sand beds. After adjusting its acidity the filtered solution is subjected to several electrochemical steps to remove copper. The remaining solution contains cobalt, some nickel, zinc, and manganese. The cobalt is then precipitated, separated by filtration, and redissolved in an acid solution and recovered by electrolysis. Resulting cathodes have a composition of 92 to 94 percent cobalt, 1 to 3 percent zinc, and small amounts of nickel, iron, copper, manganese, and sulfur. These cathodes are later melted in electric-arc furnaces and further refined, using special slags and electrodes. The molten purified metal, now over 99.15 percent cobalt, is granulated by pouring it into water.

The mixed ore concentrate, the third product from Kolwezi, contains both the oxides and sulfides of copper and cobalt. The concentrate is first treated in a Fluo-Solid sulfate-roasting furnace, where the sulfides are oxidized to soluble sulfates. The sulfates are repulped with acid solution before they are subjected to the hydrometallurgical and electrometallurgical operations described earlier for the extraction of copper and cobalt. However, a much improved and shorter process for recovery of cobalt is used at the new plant in Luilu. The new process discarded the slow electrolytic copper plating procedures in favor of removing copper with lime. A preliminary nickel removal step also was added to the new process. In this step nickel is removed as a sulfide by the addition of sodium hydrogen sulfide. This operation shortens the circuit by removing the last traces of copper along with the nickel. Zinc is removed as zinc sulfide by the addition of hydrogen sulfide. The solution undergoes further purification and clarification before it is electrolyzed. Cobalt produced by the new process at Luilu is of sufficient purity that it needs no further refining (*14*).

The only domestic producer of cobalt is the Pyrites Co., Inc., Wilmington, Del. The raw material is from magnetite iron ore mined by Bethlehem Cornwall Corp. in Pennsylvania. After magnetic separation a pyrite flotation concentrate is made and sent to the Bethlehem Steel Co. plant at Sparrows Point, Md. The pyrite is roasted in Fluo-Solid reactors and cobalt extracted from the calcined product at Wilmington by percolation leaching. The leaching process requires about 250 hours for the average cycle. Iron, copper, and manganese impurities are removed from the solution by precipitation with sodium carbonate and filtration. The cobalt is then precipitated with sodium carbonate and chlorine, separated from the solution by filtration, and the resulting cobalt cake either calcined to the oxide with about 70 percent cobalt content or reduced to the metal with charcoal. The final metal granules or fines contain 98.0 to 99.0 percent cobalt (*7*). Over 99 percent of the soluble cobalt in the calcine is recovered.

USES

Cobalt has wide applications in many industries. The more important uses are in the manufacture of various steel alloys, permanent magnets, driers, catalysis, and high-temperature, high-strength alloys. The use of cobalt for alloys dates to the turn of the century when Elwood Haynes patented a series of cobalt-chromium alloys, which he named "Stellites". These early alloys were the forerunners of today's high-temperature, high-strength alloys or "superalloys." The special features of these alloys are their high mechanical strength at elevated temperatures and excellent resistance to corrosion by hot gases. The use of superalloys increased rapidly with the development of jet engines, rocket nozzles, and gas turbines, all of which use very hot gases. The cobalt used for these engines and other equipment for outer space accounted for about one-quarter of the total amount consumed.

Another major use of cobalt is in the manufacture of permanent magnets. The first cobalt steel for permanent magnets was developed in 1916 by Honda and Saito. It consisted of 35 percent cobalt, 6 percent chromium, 5 percent tungsten, the balance being iron and trace amounts of other elements. In 1930, Mishima discovered that iron-nickel-aluminum alloys had remarkable permanent magnet properties. A cobalt addition to these alloys was later found to improve the magnetic properties. In 1936, the General Electric Co. announced the development of the first of the aluminum-nickel-cobalt or "Alnico" series of permanent-magnet alloys. Permanent magnets have many uses. Probably the largest single use for Alnico magnets is for loudspeakers. High-fidelity recording and broadcasting of recent years have created a demand for high-quality loudspeakers which may contain Alnico magnets weighing several pounds.

In 1913, Schlesinger showed that the addition of 5 percent cobalt improves the life of high-speed tool steels. Cobalt also raises the melting point of these steels and increases the carbide solubility in austenites. Moreover, the addition of cobalt to an alloy diminishes the tendency to grain growth, retards tempering after quenching, and inhibits the precipitation and coalescence of carbides. For these reasons and others, cobalt has been found particularly useful when the cutting edge of any tool is subjected to high temperature.

Driers are substances used to increase the rate and completeness of the drying of paints, varnishes, lacquers, enamels, and similar materials. Specifically, driers act by catalyzing the polymerization of the oils contained in the paints. All driers are essentially organometallic compounds, chiefly of cobalt, manganese, and lead. Although the cost of cobalt is higher than the other metals used, it is by far the most effective. Because of this superiority, cobalt is used either alone or with other metals.

There are two major categories of cobalt driers, fused and precipitated. The classification is derived from the method of preparation. The fused type is made by adding cobalt hydroxide to rosin at high temperatures. The precipitated type is formed by reacting soluble salts of cobalt with those of the desired organic acids. Fused driers are somewhat variable in composition, and in recent years they have been widely supplanted by precipitated driers on account of their greater efficiency and uniformity. Cobalt resinates and naphthenates are widely used precipitated driers. Other cobalt compounds used for driers in recent years are cobalt octoates, lineolates, and tallates.

In addition to the catalytic activity as a drier, cobalt in form of metal, oxide, or salt is used as a catalyst in many reactions such as hydrogenation, hydration, desulfurization, oxidation, and reduction. Since the oxides are very effective oxidizing agents, they have been a subject of extensive investigation in recent years as possible antismog devices.

A relatively new application for cobalt is in the oxo reaction, which involves the catalytic addition of carbon monoxide and hydrogen to an olefin to form aldehydes, which are reduced to alcohols in the second stage of the reaction.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Current world cobalt production is derived entirely from ores of other metals, principally copper and nickel. This relationship is likely to persist, as there are few large deposits containing cobalt as the principal mineral. However, copper, nickel, and gold have been recovered from the cobalt ore mined in Idaho, and nickel and gold are recovered from cobalt ore at the Bou-Azzer mine in Morocco.

ALTERNATE MATERIALS

Although nickel is less efficient in some uses, it can be readily substituted for cobalt in other uses without appreciably altering the desired properties. For example, nickel can be substituted as a binder in cemented carbides and in armor-piercing projectiles. Moreover, a nickel-base alloy, free of or containing only a low cobalt content, can be used as a substitute for some cobalt-base high-temperature alloys.

With some loss of cutting speed and production rate, high-speed tool steels may be substituted for the more expensive tools with high cobalt content.

Alnico magnets can be replaced with bismanol magnet alloy consisting of bismuth, manganese, and powdered iron, or by barium ferrite materials. Bismuth is more expensive than cobalt, however.

Although cobalt driers show the most rapid drying time of all the metal driers, manganese, lead, and iron can be used as substitutes.

SECONDARY SOURCES AND RECOVERY

Very little published material is available concerning the generation, collection, and disposition of secondary cobalt-bearing materials. The average amount of contained cobalt derived from secondary sources during 1959–63 is estimated at about 226,000 pounds per year. Superalloy scrap probably accounts for the bulk of secondary cobalt supply, owing to the fact that current engineering specifications require high-temperature, high-strength material, and components made from such alloys, notably turbine buckets and jet engines, have a relatively brief service life.

Although the permanent magnet industry consumes about the same amount of cobalt annually as does the superalloy industry, the service life of permanent magnets is relatively long. Therefore, magnet scrap probably plays a very minor role in the cobalt scrap supply.

Other possible sources of secondary cobalt are spent catalysts and other nonmetallic alloy scrap. Such materials are much more widely distributed than the metallic types; for this reason it is correspondingly more difficult to collect data concerning them.

RESERVES

The largest recoverable cobalt reserve is in Katanga Province, Republic of the Congo. The primary cobalt ore is found in the so-called Mines Series belonging to the Upper Roan group. The primary ore deposits consist chiefly of bornite, chalcocite, and chalcopyrite, with some carrollite, linnaeite, and pyrite. Ore was originally mined from a number of small enrichments in the oxidized zone in mines near Elizabethville and Jadotville and from

mines in the Western group. These deposits contain 3 to 4 percent cobalt. Now most of the cobalt in this area is extracted from richer sulfide ores. The Union Minière du Haut-Katanga mines reserve is said by the company to contain enough cobalt for at least 80 years of production at an annual rate of 19 million pounds, or about 750,000 tons.

The deposits of Katanga and Northern Rhodesia are geologically in a single mineral district. The ore reserves of Northern Rhodesia have an indicated content of 375,000 tons of cobalt. Elsewhere in Africa, the cobalt-nickel deposits of Bou-Azzer and El Graara, Morocco, are about 105 air-miles southeast of the railroad junction at Marrakech. The Moroccan ore consists mostly of skutterudite, interlaced with some cobaltite, safflorite, niccolite, and several other minerals. Since little development is done ahead of actual mining in this district, ore reserves can only be inferred. Very rough estimates place the reserve at about 800,000 tons with an average of 1.6 percent cobalt content, or a total of about 13,000 tons of metal.

Although the nickel and cobalt deposits in New Caledonia were discovered in 1864, exploitation of these deposits for cobalt did not commence until 20 years later. Cobalt is present in all of the New Caledonian nickel ore in varying amounts. The laterite layer, containing the bulk of the cobalt, has up to 0.5 percent of it, and some rich deposits may contain as much as 5 percent. The average cobalt content of the ore is around 0.2 percent. The Société le Nickel, and firm which controls most of the New Caledonian ore, reported that the known cobalt ore reserve on the firm's property is 220 million tons (*1*).

The immense nickeliferous laterite deposits in Oriente Province, Cuba, probably constitute the largest potential reserve of cobalt in the Western Hemisphere. According to Bureau of Mines estimates, the ore deposits so far prospected in the Levisa Bay, Moa Bay, Toca Bay, and Mayari districts of Oriente Province together with the Plateaus Cajabanes deposit of Pinar del Rio Province contain a total of 370,000 tons of cobalt in ore which averages over 1 percent nickel and 0.1 percent cobalt. In addition, there is a potential reserve of lower grade material with less than 1 percent nickel and about 0.07 percent cobalt containing about 1.2 million tons of cobalt.

There are a number of sources of cobalt in Canada. The Sudbury district, Temiskaming silver-cobalt area, Lynn Lake, and Thompson have the largest deposits. The nickel-copper ore of the Sudbury district and of Thompson, both owned and operated by the International Nickel Co., contain only small amounts of cobalt, variously estimated at 0.06 to 0.1 percent. These deposits constitute the largest known reserve of cobalt on the North American Continent. Cobalt occurs in the ores as a complex mixture of cobalt-nickel-iron arsenides closely associated with pentlandite. The total nickel ore reserve in these two areas at yearend 1963 was about 300 million tons, which would mean a cobalt reserve of about 180,000 to 300,000 tons.

Falconbridge Nickel Mines, Ltd., also has mining operations in the Sudbury district. At yearend 1963, Falconbridge had a proven nickel-copper ore reserve of 27 million tons and an indicated cobalt reserve of about 40,000 tons. The Lynn Lake, Manitoba, nickel-copper ore of Sherritt Gordon Mines, Ltd., contains small amounts of cobalt. Nickel concentrate produced from the ore contains about 12 percent nickel and 0.4 percent cobalt. The reserves of the company total 12 million tons of ore with an average nickel content of 0.94 percent. Assuming the same nickel-cobalt ratio exists in the ore as exists in the concentrate, this would give a cobalt reserve of approximately 3,700 tons.

The United States does not have large minable cobalt reserves. The largest known deposit of high-grade cobalt ore is in the Blackbird district of Lemhi County, Idaho. The former operator of this mine, Calera Mining Co., stated that the measured and indicated reserve contained 7,500 tons of cobalt, where as the inferred reserve is estimated to be about 15 to 20 times larger. The cobalt-bearing lead ores near Fredericktown, Mo., mined at one time by the National Lead Co., constitute another sizable deposit of cobalt ore in the continental United States. Estimated reserves total about 2 to 3 million tons of ore with an average cobalt content of 0.3 percent (*1*).

The cobalt-bearing iron ore deposits of the Bethlehem Cornwall Corp., Cornwall, Pa., the sole domestic cobalt producer, probably constitutes the second largest cobalt reserve in the United States. The large ore bodies contain 40 to 60 percent magnetite and about 3.5 percent pyrite. The pyrite fraction contains 1.5 percent cobalt. Thus, the ore contains an average of about 0.05 percent cobalt (*1*).

SOURCES OF STATISTICAL INFORMATION

The Bureau of Mines obtains monthly data on production and stocks of cobalt from domestic producers; monthly data on production and stocks of cobalt products by forms from all refiners; and monthly data on consumption by forms and end use and on stocks from virtually all consumers. World production data are compiled from State Department dispatches and of-

ficial publications of foreign countries, and figures on foreign trade are obtained from the Bureau of the Census. The Bureau of Mines publishes monthly reports on cobalt and a comprehensive annual report for use by industry and government.

PRODUCTION, CONSUMPTION, AND TRADE

The Republic of the Congo produced 63 percent of the 1963 world cobalt output, and Morocco ranked second, producing 12 percent of the total. The United States consumes approximately 30 to 40 percent of the free world cobalt production.

The Republic of the Congo continued to be the main source of U.S. cobalt imports, providing about one-half of all the cobalt imported in 1963. Belgium, West Germany, and Norway composed the next large group, providing 14, 13, and 10 percent, respectively, of the total. France, Canada, and the remaining countries provided 7, 6, and 3 percent, respectively.

The United States exported a total of about 4,500 tons of cobalt-bearing materials during 1959–63. Scrap, defined as material having at least 5 percent cobalt content, was the chief cobalt-bearing item. Exports of fabricated and semifinished items totaled a little over 250 tons during 1959–63. Shipments to Japan and West Germany were by far the largest.

Cobalt metal and ore continued to enter the United States duty free. Effective July 1, 1963, the duty was reduced on cobalt oxide from 2.7 cents to 1.5 cents per pound, and reduced on the sulfate, from 2 cents to 1.5 cents per pound; the duty on other cobalt salts and compounds, not specially provided for, was reduced from 13.5 percent to 12 percent ad valorem. The duty on cobalt lineolate was increased from 5 cents to 7.25 cents per pound (*16*).

TABLE 3.—*Production of cobalt products in the United States*

[Short tons]

Year	Metal		Oxide		Hydrate		Salts		Driers	
	Gross weight	Cobalt content	Gross weight	Cobalt content	Gross weight	Cobalt content	Gross weight	Cobalt content	Gross weight	Cobalt content
1954–58 (average)	1,987	1,934	259	184	165	86	587	165	4,806	282
1959	1,239	1,231	117	82	100	57	552	156	6,681	384
1960	775	770	259	181	95	54	628	193	6,167	356
1961	(1)	(1)	219	153	113	52	605	165	5,181	304
1962	(1)	(1)	229	160	139	74	753	216	4,359	273
1963	(1)	(1)	212	149	223	108	797	238	4,583	286

[1] Figures withheld to avoid disclosing individual company confidential data.

TABLE 4.—*World mine production of cobalt, by countries*

[Short tons of contained cobalt]

Year	United States	Congo (Leopoldville)	Canada	Northern Rhodesia	Morocco	Other countries	Total [1]
1954–58 (average)	1,315	9,013	1,553	1,300	775	1,143	15,100
1959	1,165	9,294	1,575	2,270	1,330	207	16,300
1960	(2)	9,063	1,784	2,036	1,401	82	15,700
1961	(2)	9,178	1,591	1,701	1,422	14	14,800
1962	(2)	10,674	1,741	951	1,583	199	15,900
1963	(2)	8,050	1,408	778	1,511	210	12,700

[1] Cobalt is also recovered, principally in West Germany, from pyrites produced in Finland, and estimates are included in the world total. Production data for Bulgaria, East Germany, Poland, and U.S.S.R. are not available, and no estimates for these countries are included in the world total. Cobalt concentrates are being stockpiled in Uganda, but exact figures are not available.

[2] Figures withheld to avoid disclosing individual company confidential data; U.S. figures included in world total.

TABLE 5.—*Cobalt consumed in the United States, by uses*

[Short tons of contained cobalt]

Use	1954–58 (average)	1959	1960	1961	1962	1963
Metallic:						
High-speed steel	96	107	78	110	171	202
Other tool steel	60	309	26	22	32	69
Other alloy steel			287	270	273	349
Permanent-magnet alloys	1,299	1,490	1,194	1,228	1,433	1,176
Cutting and wear-resisting materials	107	70	131	128	158	138
High-temperature, high-strength alloys	1,376	1,212	1,012	1,177	1,508	1,227
Alloy hard-facing rods and materials	245	202	224	275	325	303
Cemented carbide	113	169	160	149	305	204
Nonferrous alloys	126	327	53	73	64	79
Other			248	330	291	213
Total	3,422	3,886	3,413	3,762	4,560	3,960
Nonmetallic (exclusive of salts and driers):						
Ground-coat frit	243	272	233	263	267	290
Pigments	107	100	95	96	84	111
Other	66	127	139	157	237	303
Total	416	499	467	516	588	704
Salts and driers: Lacquers, varnishes, paints, inks, pigments, enamels, glazes, feed, electroplating, etc. (estimated)	498	566	586	520	486	601
Grand total	4,336	4,951	4,466	4,798	5,634	5,265

TABLE 6.—*U.S. imports for consumption of cobalt, by classes*

[Short tons]

Year	Gross weight					Total	
	White alloy [1]	Ores and concentrates [2]	Metal	Oxide	Salts, other compounds	Gross weight	Cobalt content (estimated)
1954–58 (average)	1,770	25	[3, 4] 7,345	382	171	9,692	8,370
1959		[3] 386	10,044	779	139	11,347	10,623
1960		[3] 3,231	5,400	730	115	9,476	6,085
1961			5,018	340	80	5,438	5,248
1962		[3, 5]	[6] 5,905	489	60	[6] 6,454	6,217
1963		15	5,161	234	47	5,457	5,261

[1] Reported by importer to Bureau of Mines, which adjusted the figures for "ores and concentrates" for 1954–58, as reported by the Bureau of the Census, to exclude "white alloy" from the Republic of the Congo.
[2] Figures exclude receipts of "white alloy" from the Republic of the Congo.
[3] Adjusted by the Bureau of Mines.
[4] Includes scrap.
[5] Less than 1,000 pounds.
[6] Revised figure.

Source: Bureau of the Census.

STRATEGIC CONSIDERATIONS

The major suppliers of cobalt to the United States are the Republic of the Congo, Belgium, and Canada. The refinery in the Republic of the Congo is about 1,200 miles by rail from the Atlantic port of Lobito in Angola. Shipments are made from Lobito to the United States. The principal cobalt refinery in Canada is at Port Colborne, Ontario, about 20 miles from Buffalo, N.Y. Other large refineries supplying cobalt to the United States are in France, Norway, United Kingdom, and West Germany.

PRICES

Since the last change in price on March 1, 1960, the price of cobalt metal granules and regular fines has been $1.50 per pound, f.o.b. carrier, Niagara Falls, N.Y., New York, N.Y., and Chicago, Ill., packed in 500-pound drums. The prices of ceramic-grade cobalt oxides with 70 to 71 and 72.5 to 73.5 percent cobalt content are $1.12 and $1.15 per pound, respectively. Above oxide prices are quoted for 250 pound kegs delivered east of the Mississippi River. For deliveries west of the Mississippi River, 3 cents per pound is added.

TABLE 7.—*Prices per pound of cobalt metal and cobalt oxide in the United States* [1]

Year	Date of change in price	Cobalt metal f.o.b. Niagara Falls or New York, N.Y., Chicago, Ill.	Cobalt oxide, ceramic grade east of Mississippi River (gross weight)
1940–46		$1.50	$1.16
1947	July 1, 1947	1.65	1.27½
1948		1.65	1.27½
1949	Apr. 1, 1949	1.80	1.38
1950		1.80	1.38
1951	Jan. 1, 1951	2.10	1.60
	Oct. 1, 1951	2.40	[2] 1.76
1952		2.40	1.82
1953	Nov. 1, 1953	2.60	1.96
1954		2.60	1.96
1955		2.60	1.96
1956	Dec. 1, 1956	2.35	1.78
1957	Feb. 1, 1957	2.00	1.52
1958		2.00	1.52
1959	Feb. 1, 1959	1.75	1.33
1960	Mar. 1, 1960	1.50	1.14
1961		1.50	1.14
1962		1.50	1.14
1963		1.50	1.14

[1] E&MJ Metal and Mineral Markets.
[2] Price change Nov. 1, 1951.

TAXES

Domestic cobalt producers are granted a depletion allowance of 23 percent on income from domestic production and 15 percent on income from foreign production.

In addition to a 15-percent depletion allowance (of salable value of minerals), taxable incomes of operations outside the United States and within the Western Hemisphere are taxed at 14 percentage points below the U.S. corporate income tax rate. With an appropriate rate of 48 percent for domestic operations, the rate for Western Hemisphere trading corporations is approximately 34 percent.

RESEARCH

Bureau efforts in research and development consist of technical and economic feasibility studies of some potential sources of cobalt, and various metallurgical processes for some minerals containing cobalt. Research is also directed toward investigating the chemical and physical behavior of certain compounds and alloys of cobalt. Results of several investigations indicated an improved process of preparing high-quality cobalt and nickel (*12*, *9*, *4*).

The Centre d' Information du Cobalt (Cobalt Information Center), Brussels, Belgium, sponsors many research and development efforts in all phases pertaining to cobalt. Results of one series of investigations dealt with a number of refractory metals and cobalt (*8*). The Center published articles concerning the chief function of cobalt in heat-resisting alloys (*2*) and the oxidation resistance of a number of cobalt-base alloys (*3*). The Center also published two comprehensive, detailed articles on the analytical chemistry of cobalt (*15*).

Despite recently introduced refractory metals and their alloys for high-temperature, high-strength applications, much research continues on the less-expensive cobalt-base superalloys. The Defense Metals Information Center (DMIC), Battelle Memorial Instiute, Columbus, Ohio, recently published a detailed report on various conditions that affect the behavior of cobalt-base superalloys (*17*). DMIC studies also included a compilation of tensile properties of high-strength alloys including cobalt-base superalloys (*5*). Martin Metals Co. produced a high-temperature cobalt-base alloy, designated as SM302. It was developed for use in the first turbine stage of modern turbojet engines. Another cobalt-base alloy, SM322, was developed for use as a turbine-blade material. A new series of cobalt-refractory-metal alloys was announced for advanced space vehicles by the National Aeronautics and Space Administration (NASA). Cobalt-base alloys with refractory metals as the major alloying constituents were found to be especially suited in reducing material loss by evaporation in the ultra-high-vacuum environment of outer space (*10*). A program on the development of coated thin-sheet superalloy components has been in progress at Bell Aerosystems Co. (*13*).

A number of new cobalt products that may find wide applications in the future have been reported. Allegheny Ludlum Steel Corp. developed a new high-strength, precipitation-hardening stainless steel, designated as AM–367. The Forging and Casting Division of Allegheny Ludlum Steel Corp. developed an alloy under the designation of ALX–6. The new alloy was a cobalt-base metal designed primarily for applications that require high resistance to thermal shock and heat checking. Kanthal Corp. announced the development of an iron-chromium-aluminum-cobalt, electrical-resistance alloy, known as Kanthal D. Bethlehem Steel Co. developed an improved hot-work, tool steel for high-temperature operations. The alloy, Chromo-Co, is essentially the same as the firm's Chromo-N, to which 10 percent cobalt has been added. Westinghouse Electric Corp. introduced a new wrought, highly ductile, improved magnetic alloy under the name of Vicalloy. The new alloy, with a 52-percent cobalt content, can be fabricated into various shapes. Russian metallurgists have developed a lower cost, creep-resistant material to replace their designated LK4 alloy. The new alloy has less than 2 percent cobalt compared with 60 percent in the LK4 alloy. Prop-

erties of the new alloy compared favorably with those of the more expensive LK4 alloy.

Sherritt Gordon Mines, Ltd., developed five closely sized grades of very pure cobalt powder for powder-metallurgy applications. Girdler Catalyst Division of the Chemetron Corp. introduced a cobalt catalyst, designated as G–61, which has a high degree of selectivity in reducing certain nitriles to amines.

Several recently developed coating and plating processes promise wide application. Stellite Co., division of Union Carbide Corp., announced the development of four new metallic diffusion coatings. Designated as C–9, C–10, C–11, and C–12, the new alloys are expected to be used on copper and cobalt-base alloys. Lockheed Missiles & Space Co. reportedly developed two new metal plating processes that produce thin ferromagnetic films of almost pure metal, including cobalt on both metallic and nonmetallic bases. Selectrons, Ltd., was said to have developed a modified selective plating technique which may reduce costly rejections of machined parts. Called the Flow-Plating technique, the process appears to have potentially extensive applications. Several metals, particularly cobalt, were said to be specially suited for the new plating technique.

OUTLOOK

Free world cobalt-producing capacity will continue to exceed free world consumption. Consequently, there will be a surplus of cobalt for the foreseeable future. The surplus may be aggravated by the strong demand for copper, which will lead to increased production from cobalt-bearing copper ores.

To bring production and consumption more in balance, new specific uses for cobalt may come from an expanded program of research in new applications and in the development of new products. These new uses may, in turn, result in an increased demand for the metal. In this regard, the outlook for expanding the use of cobalt in permanent magnets, high-temperature, high-strength materials, and other ferrous and nonferrous cobalt alloys is encouraging. Recent research and development efforts have proved successful in improving several methods of extraction of the metal from ores and also in producing cobalt of very high purity. Continued success in these fields eventually will lower the production cost of cobalt to the extent that it may become competitive with less-expensive alternate materials.

The domestic cobalt supply position, however, could be improved greatly by the discovery and development of new and better methods in concentrating, extracting, and producing the metal from domestic low-grade ore and other raw materials. Such technological innovations and improvements would lower the cost of domestic production and provide an incentive to establish a domestic source of cobalt. The domestic supply position could also be enhanced by greater recovery and utilization of cobalt-bearing scrap.

The prospect of finding large deposits of commercial-grade cobalt in the United States is not promising. Hence, for an indefinite period the United States will continue to depend on foreign sources for the greater part of its cobalt needs.

PROBLEMS

High price is one of the major obstacles restricting the use of cobalt in alloy steels in favor of cheaper metals. Nickel, costing about one-half as much as cobalt, is notable among the alternates which impart to alloys chemical and physical properties comparable to those of cobalt alloys. There are other less-expensive substitutes for cobalt which do not alter too much the desired properties of alloys. Furthermore, even where requirements specificially call for cobalt, efforts are made to minimize the amount used. Attributed to the cost of recovery and refinement, the high price of cobalt promises to remain an obstacle to its use.

Although there is some research and development devoted to the expansion of the cobalt market in some particular fields, there is actually no large-scale research and development program to expand cobalt's application; especially, those uses that may require large quantities of the metal. Such a program would also fill a need for basic information pertaining to cobalt. The lack of data on the physical metallurgy of the element, for example, hinders the development of new alloys. Such data are also needed to explain cobalt's precise role in the alloying and other metallurgical processes. A case in point is that of high-temperature, high-strength alloys.

Complete removal of cobalt from engineering materials for atomic and nuclear applications still remains a problem. More efficient recovery of cobalt as a separate product from laterite and serpentine ores and other raw materials

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with low cobalt content is another problem. Much effort could also be devoted to reclaiming high-temperature, high-strength alloy scrap. A simple, quick, and inexpensive field method for identifying and classifying cobalt-bearing scrap material would be of considerable aid.

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COLUMBIUM

By Richard F. Stevens, Jr.[1]

ALTHOUGH discovered in 1801, columbium did not find significant commercial application until the 20th century. It was first used as an alloy constituent in steels, and this continues to be the metals major volume usage. Pure columbium metal and nonferrous columbium-base alloys currently are used in nuclear reactors and in heat- and corrosion-resistant applications in jet engines, missiles, supersonic aircraft, and space capsules. Magnets of superconducting columbium compounds are being used in attempts to control fusion reactions.

Although no domestic production of columbium ores or concentrates was reported from 1960 through 1963, the United States has been the world's largest consumer of columbium ores and the largest producer and consumer of columbium metal and ferrocolumbium. The demand for columbium metal and ferrocolumbium is expected to increase in response to the growing steel industry and the demand for materials possessing elevated-temperature strength properties for use in space- and nuclear-age technology. Continued research will be required to develop less costly processes for all phases of columbium metallurgy in order to meet the purity and cost specifications expected for advanced high-temperature uses.

Several million tons of columbium have been reported in low-grade complex oxide minerals and in titanium ores. Economic methods for recovering the columbium in these ores will have to be developed if they are to be utilized to meet expected demands.

BACKGROUND

During the 1930's columbium came into use as a steel-alloying element in the form of ferrocolumbium and as a carbide in high-speed cutting tools.

Ore shortages and increased demand for ferrocolumbium during World War II resulted in temporary allocation controls. By the end of World War II, new nonferrous columbium-bearing alloys were being used in jet engines. Shortages were again encountered during the Korean war, and in 1952 a Government-guaranteed purchase program was instituted to encourage increased production of columbium-tantalum concentrates. The desired results were achieved, and new low-grade deposits of columbium minerals were found. Termination of Government purchases of foreign columbium concentrate in May 1955 and of domestic columbite in December 1958 resulted in lower ore prices, followed by reduced production of concentrate. Industrial demand, however, began to increase for the mineral as new firms began production of the metal. This was encouraged by orders for columbium metal and columbium-base alloys to be used in nuclear-reactor research, and by the promise of columbium-bearing high-temperature alloys for jet engines, gas turbines, high-speed aircraft, and missiles.

SIZE AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Columbium mining has been predominantly a foreign industry. Nigeria, Malaysia, Congo (Leopoldville), Norway, Canada, and Brazil are the principal ore-producing countries. Domestic mine output until 1956 consisted of intermittent and highly variable production from many pegmatite deposits in South Dakota, Colorado, New Mexico, Maine, New Hampshire, and North Carolina, with minor production

[1] Commodity specialist.

from a few other States. In 1956, production started from euxenite-columbite-monazite placer deposit in Bear Valley, Idaho, and continued into 1959. Since 1960 there has been no domestic production of columbium concentrate.

The present refinery capacity in the United States is estimated to be more than 300 tons of columbium. This is several times the installed capacity of the rest of the free world.

Columbium metal, compounds, or alloys were produced during 1963 by E. I. Du Pont de Nemours & Co., Inc., Newport, Del., and Baltimore, Md.; Fansteel Metallurgical Corp., North Chicago, Ill., and Muskogee, Okla.; Kawecki Chemical Co., Boyertown, Pa.; Kennametal Inc. Latrobe, Pa.; Stauffer Chemical Co., Richmond, Calif.; Union Carbide Metals Co., Niagara Falls, N.Y.; Union Carbide Stellite Co., Kokomo, Ind.; and Wah Chang Corp., Albany, Oreg.

Some foreign firms reported as producing columbium metal, compounds, or alloys follow: Canada—St. Lawrence Columbium and Metals Corp.; England—Murex Ltd., Blackwell's Metallurgical Works Ltd., Minworth Metals, Ltd., and London and Scandinavian Metallurgical Co., Ltd.; Belgium—Fansteel-Hoboken, S.A.; France—Fabriques de Produits Chimiques de Thann et Mulhouse S.A., and Société d'Électrométallurgie d'Ugine; Germany—Herman C. Stark A.G., Heraeus Quarzschmelze, and Gesellschaft für Électrométallurgie; Austria—Metallwerke Plansee; Switzerland—Société des Produits Pharmaceutiques Ciba; Finland—Kovametalli Oy; Italy—S.P.A. Leghe è Metalli; Japan—Showa Denko K.K., Tokyo Electrolysis Co., Ltd., and Japan Vacuum Engineering Co., Ltd.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Columbium is a silver-gray, lustrous metal about as hard as copper. It is characterized by high melting point, resistance to corrosion, and ease of fabrication. At elevated temperatures the metal is an excellent interstitial absorber of common gases, but the massive metal rapidly becomes coated with a nonvolatile oxide which retards deeper penetration. It is a relatively good conductor of heat and electricity and an excellent thermionic emitter of electrons in vacuum tubes. It has about the same density as steel and a relatively low thermal-neutron-capture cross section of 1.1 barns.

The name "columbium" was proposed in 1801 when Hatchett, an English chemist, discovered a new metallic oxide in a mineral from the United States (Columbia). In honor of the land of its origin, he named the new element columbium and the mineral which contained it columbite. The following year, the Swedish chemist, Ekeberg, isolated what he thought was a new element and named it tantalum, after Tantalus a minor god of Greek mythology, because of the way it had tantalizingly kept its identity from his grasp for many years. In 1844 Rose concluded that Ekeberg's material had really been a mixture of two elements and named the second niobium in honor of Niobe, the daughter of Tantalus. In 1866 Marignac determined that Hatchett's columbium and Rose's niobium were the same, but to this day the dual nomenclature for the element has continued.

Columbite is marketed on the basis of a minimum of 65 percent combined columbium and tantalum pentoxides in specified ratios of Cb_2O_5 to Ta_2O_5, generally 10 to 1 or 8½ to 1.

Columbium is sold in many grades, ranging from a technical-grade metal of 95 percent purity to nuclear-grade metal more than 99.9 percent pure.

Ferrocolumbium usually is sold on a basis of 50 to 60 percent columbium, maximum 0.40 carbon, and maximum 8 percent silicon. Material containing about 70 percent columbium also is marketed.

Ferrotantalum-columbium contains at least 20 percent tantalum and 40 percent columbium.

National stockpile purchase specifications for columbite are based on three grades. Grade A requires 65 percent combined pentoxides with a minimum ratio of Cb_2O_5 to Ta_2O_5 of 10 to 1. Grade I requires 60 percent combined pentoxides with a minimum ratio of Cb_2O_5 to Ta_2O_5 of 8½ to 1. Grade II requires 55 percent combined pentoxides with a minimum ratio of Cb_2O_5 to Ta_2O_5 of 1 to 1.

TECHNOLOGY

Geology

The percentage of columbium in the crust of the earth has been estimated at 0.0024 percent (*17*).[2] The principal columbium minerals are pyrochlore, fergusonite series, tapiolite-mossite series, columbite-tantalite series, euxenite-polycrase series, eschynite-priorite series, betafite series, samarskite, and columbian perovskite.

Originally the major source of columbium was from minerals of the columbite-tantalite series recovered from pegmatite deposits and residual and placer deposits derived from the weathering of pegmatites or granites. Currently, however, the major source of columbium is the pyrochlore minerals which occur associ-

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

ated with alkalic rocks in pegmatites, nepheline syenite, various alkalic dike rocks, carbonatites associated with alkalic intrusives, extrusive alkalic rocks, greisen, and in decomposed products of these rocks. Pyrochlore is generally brown or black in color and has a specific gravity of 4.2.

Many carbonatite bodies are reported to contain columbium, titanium, zirconium, rare-earth metals, barium, strontium, uranium, magnetite, phosphate, vermiculite and agricultural-grade limestone.

Columbium minerals occasionally are associated with cassiterite or gold in veins. Characteristic geochemical associations are most often with tantalum, rare-earth elements, titanium, zirconium, and tin (*17*).

Mining

Depending upon local labor and power supply and the geologic nature of the deposit, mining methods extend from native hand labor to giant dredges and highly mechanized open pit mining operations. Underground mining is restricted to relatively shallow inclines and shafts which have followed rich ore shoots beyond the practical limit of open cut mining techniques.

Metallurgy

Concentration

Columbium-tantalum concentrate is produced by hand sorting, by various combinations of gravity, magnetic, and electrostatic separation, or by chemical means. Flotation methods, used only in Norway at present, may be useful in future treatment of pyrochlore ores.

Extraction and Separation of Compounds and Reduction to Metal

Columbium and tantalum are very similar chemically, and complete separation of the two is very difficult. The classical method for extracting columbium and tantalum from their ores is by fusion with hot sodium hydroxide followed by leaching with water and with hydrochloric acid to remove impurities. The columbium-tantalum residue is dissolved in anhydrous hydrogen fluoride, and potassium hydroxide is added. Upon cooling, potassium-tantalum fluoride precipitates, leaving more soluble potassium-columbium oxyfluoride in solution. The columbium solution is then passed through an involved series of steps including precipitation, solution, fractional crystallization, washing, and calcining to produce columbium pentoxide. Solvent extraction methods, perfected by the Bureau of Mines, are also used commercially to separate columbium and tantalum oxides. The solvent extraction system, hydrofluoric acid-sulfuric acid-methyl isobutyl ketone, will yield more than 90 percent of the contained columbium and tantalum values, free of each other and all metallic impurities, regardless of the columbium-tantalum ratio in the starting material. Chlorination of ferrocolumbium with subsequent separation of pure columbium chloride by fractional distillation is a third technique.

Euxenite from Idaho was processed by Mallinckrodt Chemical Works, St. Louis, Mo. The concentrate was digested with hot sodium hydroxide, washed, leached with hydrochloric acid, and filtered. The residue contained columbium, tantalum, and some impurities, while the filtrate contained uranium, thorium, rare-earth elements, and iron. By dissolving the columbium-tantalum residue and reprecipitating it several times under close pH control, the columbium-tantalum oxides were separated from impurities.

Columbium metal is usually prepared from briquets made from the pentoxide in a stoichiometric ratio with columbium carbide. The briquets are heated in a vacuum to above 1,600° C, the carbon and oxygen forming carbon monoxide. The remaining columbium metal is fed to a ball mill and ground to a fine powder. Other reduction methods include bomb reduction of the oxide with calcium and iodine and Kroll process reduction of columbium chloride.

Columbium powder is pressed into porous bars and sintered in a high-vacuum furnace in one method of producing ingot. The bars are heated by passing an electric current through them for several hours. Other methods of producing pure consolidated ingot include consumable-electrode vacuum arc melting, zone melting, and electron-bombardment melting. This last technique permits a remarkable degree of purification and will probably be of increasing importance. Levitation melting is used experimentally.

Use Technology

Columbium is added to steel in the form of ferrocolumbium or ferrotantalum-columbium, both of which are less expensive than the pure metal. The ferroalloy may be manufactured in two ways. In the electric furnace method, columbite ore, silicon or silicon alloys, and fluxing agents form the furnace charge. Both slag and metal are tapped at a temperature above 1,600° C. In the aluminothermic method, the ore must be carefully dressed before smelting to eliminate associated minerals that would be deleterious to the final product. The charge consists of the refined concentrate, aluminum powder, and oxidizing agents such as sodium

chlorate and barium peroxide. The reaction is started by igniting a small quantity of aluminum powder and barium peroxide on top of the charge.

In preparing columbium carbides, the metal powder may be carburized directly by mixing with a stoichiometric quantity of carbon and heating slowly to 2,000° C in hydrogen or in a vacuum, by firing a mixture of powdered metal and carbon in a closed graphite tube in a hydrogen atmosphere at about 1,600° C, or directly from ore or oxides by smelting with carbon and various molten metallic solvents, such as aluminum, and then purifying the resultant carbide crystals by acid treatment of the regulus to remove aluminum and aluminum carbide. Columbium oxides also will react with lampblack at about 1,900° C in an inert atmosphere to form carbides. A German method sinters a mixture of iron, tantalum, and columbium powders with carbon. The sinter is powdered, leached with hydrochloric acid, heated to 1,600° C for 2 hours, and again powdered and leached with dilute hydrochloric and hydrofluoric acid to remove final traces of iron.

Columbium fabrication and working are affected by several characteristics of the metal. Since the metal, when hot, readily absorbs gases that cause embrittlement, all forming, stamping, and drawing are done cold or in an inert atmosphere. The metal also seizes and tears easily so that caution must be used during machining. Columbium is comparable with mild steel in its ability to be drawn, stamped, or formed. Columbium work hardens at a much slower rate than most other metals, and reduction in thickness of 60 percent or more, without an intermediate anneal, is standard practice. Columbium can be welded to a number of other metals by either resistance welding or inert-gas arc welding. For welding the metal to itself, however, arc welding is used exclusively. Oxygen and other common gases must be excluded from the weld zone. Because of its tendency to oxidize at elevated temperatures, columbium must be protected during arc welding with an inert atmosphere of helium or argon.

USES

Ferrocolumbium (50–70 percent columbium) or ferrotantalum-columbium (approximately 40 percent columbium and 20 percent tantalum) is added to some austenitic stainless steels. About 1 percent columbium and tantalum will act as a carbide stabilizer. Columbium also increases the strength and impact properties of low-carbon and low-alloy steel. It is also a useful constituent with aluminum in the nitriding of steels. Uses of columbium- or tantalum-bearing steel include aircraft engine exhaust systems, welded equipment for the chemical, oil, and food industries, heavy construction equipment, and aircraft landing gear. Examples of columbium-bearing steels are type 347, 19–9WX, Croloy 15–15N, and GLX–W. Columbium-bearing electrodes are used for welding stabilized stainless steels.

Columbium is added to special steels and nonferrous "superalloys" in quantities up to 5 percent for use at elevated temperatures. Examples of such alloys are S–816, Inconel–X, MST–821, and Gamma-Cb. New columbium-base alloys have recently been marketed, such as Du Pont 80–Cb, 10–Mo, 10–Ti, Fansteel 80 and 82, and General Electric F–48 and F–50. Jet engines, automotive gas turbines, research programs on nuclear- and rocket-powered aircraft, and missiles all use such alloys.

British Standard aluminum casting alloy LM 7 specifies 0.05 to 0.30 percent of columbium and titanium. Columbium acts as a grain refiner in these alloys for use in cylinder blocks and crank cases.

Columbium is sometimes used as a getter and electron emitter in electronic tubes. In addition to ability to absorb and hold the residual gases when heated, the metal offers a high melting point, ease of fabrication, and efficient thermionic electron emission. A new type of miniature electronic valve, the cryotron, consists of a tiny strip of tantalum around which a fine columbium wire is wrapped. The combination becomes superconductive in a bath of liquid helium at about −270° C. Such a component has a considerably lower power consumption than a thermionic valve, and a hundred such devices will fit into a thimble. They offer revolutionary possibilities for computer design and great improvement in radar devices.

Columbium metal is used as a fuel-alloying element in the Experimental Boiling Water Reactor, Argonne, Ill., and as fuel cladding in the reactor at Dounreay, Scotland. Columbium, with a neutron-absorption cross section of 1.1 barns, also withstands the corrosive action of coolants and stabilizes the proportions of the fuel element. When used as a fuel-alloying element, columbium prevents violent reaction between the fuel and leaking coolant. Columbium 95 radioisotope is produced at Oak Ridge National Laboratory for use as a radioactive tracer.

Columbium carbide can be used separately or blended with tungsten and tantalum carbides and cemented with cobalt metal. Such carbides are used in hot-forging dies, cutting tools, jet engine turbine blades, valves, valve

seals, and valve guides, and for coating graphite rocket nozzles.

Columbium oxide was used during World War II as a catalyst in the production of butadiene from alcohol. The process has since been replaced by a more economical one using petroleum feedstocks that do not require the use of columbium-bearing catalysts.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Columbium in ore is usually a coproduct with tantalum and in some cases is associated with other valuable minerals such as cassiterite, mica, feldspar, beryl, and spodumene. In more intimate association, columbium and tantalum may share a crystal lattice with other valuable elements such as rare-earth metals, tin, uranium, zirconium, titanium, thorium, phosphorus, and calcium. The particular suite of valuable constituents in a given deposit often determines whether or not it can be worked profitably. Outstanding examples are the cassiterite-columbite operations in Nigeria and the euxenite-columbite-monazite ore dredged in Idaho.

Tin smelter slags and tin mine tailings are sources of columbium-tantalum. Although current practice is to separate most of the columbium-tantalum concentrates by magnetic means at the mine while the remainder of the columbite-tantalite reports with the tin concentrate, some tailing piles contain significant quantities of columbium-tantalum minerals. Tin smelter slags may contain up to 20 percent combined columbium and tantalum pentoxides.

Bauxite deposits formed from decomposition of columbium-bearing syenites, such as those in Arkansas, contain columbium-bearing minerals. Titanium plants using columbium-bearing titanium minerals as a raw material are also a potential source of columbium.

ALTERNATE MATERIALS

Acceptable but less satisfactory substitutes, such as vanadium, are available for some uses of columbium. In some stainless steels, low-carbon or titanium-stabilized steels vanadium may provide satisfactory service. For high-temperature applications, several materials are possible substitutes, including molybdenum, vanadium, or tungsten alloys, ceramics, ceramic coatings and other claddings upon less-heat-resistant alloys, and glass-reinforced plastics. In nuclear reactors columbium for fuel-element cladding is an alternate choice for materials such as zirconium, aluminum, vanadium, and stainless steel. Tantalum, zirconium, titanium, and misch metal are preferred to columbium as a getter in vacuum tubes.

Certain alloys and compounds of technetium, molybdenum, vanadium, tin, and gadolinium also have superconducting properties and could be substituted for columbium alloys and compounds to control nuclear fusion reactions.

SECONDARY SOURCES

Data are not collected on utilization of columbium scrap. However, when all scrap sources, including columbium-bearing steel scrap are considered, the quantity of columbium reclaimed for further use is important.

RESERVES AND RESOURCES

By 1960 the total cataloged columbium resource of the free world was reported to be more than 9 million tons of Cb_2O_5 (*4*). The resources occur primarily in pyrochlore, pegmatite, and placer deposits and were distributed in the following way: North America, 1.26 million tons; South America, 6.36 million tons; Europe, 42,250 tons; Africa, 1.39 million tons; and Oceania, 1,000 tons.

The total measured and inferred resource of columbium in the United States was reported to be 180,400 tons of low-grade columbium pentoxide in 1960. The reported grades ranged from 0.004 to 0.15 percent of contained oxides in the ore, too low for economical recovery using present methods of extraction.

Prior to 1955, domestic columbite-tantalite minerals were obtained entirely as a byproduct from pegmatites. Because of the highly variable columbium content of pegmatite deposits the reserves can only be inferred on the basis of the estimated volume of the deposits and the past history of columbium production from these and similar ores. The placer deposits of Idaho and the unconsolidated sediments in the Western States have an inferred reserve of 11,000 tons of Cb_2O_5. Additional resources of columbium exist in the pyrochlore deposits of Colorado. The titanium and bauxite deposits of Arkansas contain columbium in concentrations ranging from 0.05 to 0.15 percent Cb_2O_5. The red mud and black sand waste products of Arkansas alumina plants contain about 0.13 percent of columbium pentoxide which could serve as an emergency source of domestic columbium.

The largest known primary columbite resource occurs in weathered columbite-bearing granite in Nigeria. Columbium also is found in large placer and pegmatite deposits in Africa, Asia, and South America. Some tin tailings and smelter slags also contain columbium in significant quantities. The large low-grade

pyrochlore deposits of Germany, Norway, Brazil, East Africa, and Canada have been extensively explored; most of the measured resources of columbium are in these deposits.

SOURCES OF STATISTICAL INFORMATION

Data on the domestic production and consumption of columbium concentrate and production of the metal, alloys, and compounds are obtained by the Bureau of Mines through industry canvasses. Statistical data on imports and exports of concentrates and products are obtained from the Bureau of the Census, U.S. Department of Commerce. Data on world production of concentrates are compiled by the Bureau of Mines from information supplied by foreign service officers, from official publications of the Departments of Mines of foreign countries, and from other sources. Statistics on imports of columbium-tantalum-bearing tin slags or on the columbium-tantalum pentoxide content of imported concentrates are not obtained, nor are data on secondary recovery of the metals, or on consumption and use of the secondary recovered metals. There is a growing need for more complete information on consumption.

TABLE 1.—*Salient statistics of columbium*

[Pounds]

	1954–58 (average)	1959	1960	1961	1962	1963
United States:						
Columbium-tantalum concentrate shipped from mines [1]	212, 244	189, 263	----------	----------	----------	----------
Imports:						
Columbium-mineral concentrate	5, 604, 171	3, 395, 816	5, 051, 800	2, 777, 700	5, 050, 888	5, 909, 512
Columbium metal and columbium-bearing alloys	[2] 3, 602	[3] 1, 562	[3] 5, 123	2, 139	2, 875	1, 414
Exports:						
Columbium ore and concentrate	26, 181	15, 060	155, 399	56, 487	21, 330	46, 887
Columbium metal and columbium-bearing alloys	104	[4] 6, 495	[4] 21, 469	[4] 28, 930	[4] 34, 761	[4] 58, 666
Industrial consumption:						
Metal contained in raw materials consumed	820, 000	1, 190, 000	1, 538, 000	1, 738, 000	2, 844, 000	2, 054, 000
Ferrocolumbium and ferrotantalum-columbium	[5] 455, 968	565, 418	721, 487	1, 052, 181	1, 397, 638	1, 345, 789
Industrial production:						
Metal	(6)	(6)	(6)	252, 000	128, 000	104, 000
Ferrocolumbium and ferrotantalum-columbium	[7] 558, 000	709, 947	847, 968	1, 156, 051	1, 573, 915	1, 575, 943
World: Production of columbium-tantalum concentrates [8]	7, 990, 000	6, 040, 000	7, 020, 000	7, 540, 000	9, 210, 000	10, 660, 000

[1] 1956–58 data are for columbite-tantalite concentrate plus columbium-tantalum oxide content of euxenite concentrate.
[2] Average of 1956–58 only.
[3] Columbium and tantalum metal and alloys. Separate statistics for columbium are not available.
[4] Columbium and tantalum metal and alloys in crude and semifabricated forms and scrap. Separate statistics for columbium are not available.
[5] Data for 1958 only; data for previous years are unavailable.
[6] Figure withheld to avoid disclosing individual company confidential data.
[7] Average of 1957–58 only.
[8] Separate statistics for columbium ore are not available. Does not include tin slags.

PRODUCTION, CONSUMPTION, AND TRADE

Since 1940, the United States has been the world's leading consumer of columbium ores and producer of columbium-bearing products.

In 1963 the United States imported all of its columbite supply, and 68 percent of the total originated in the Eastern Hemisphere and South America.

Columium ore and concentrate, and columbium-tantalum-bearing tin slags are imported duty free. Duties on columbium-bearing metal scrap have been suspended by Public Law 869 (1950) as amended and extended. Columbian metal and alloys are dutiable at 10 percent, ad valorem, effective August 31, 1963, under the "Tariff Schedules of the United States, Annotated (1963)." For Communist nations the Statutory Rate of Duty of 25 percent, ad valorem, remains in force.

STRATEGIC CONSIDERATIONS

The quantities of columbium concentrates, compounds, and alloys stockpiled by the Government are considered to be satisfactory for

all potential emergency requirements. Foreign purchases consequently have been terminated, and no further domestic contracts are planned. Material is still acquired by barter. On June 30, 1964, inventories of stockpile-grade columbium totaled 14.2 million pounds, of which 6.0 was in the national (strategic) stockpile, 7.9 in Defense Production Act stocks, and 0.3 in the supplemental stockpile.

Domestic industry is dispersed enough to present no strategic problems.

Because of the dependence upon Eastern Hemisphere supplies, it was necessary during the peak of World War II submarine attacks to airlift high-grade ore to the United States for military uses.

Since then, however, several million tons of columbium-bearing pyrochlore have been found in Canada and Brazil and lesser quantities in the United States. In 1963, 32 percent of the U.S. columbite supply was imported from Canada. Western North American black sands, particularly in Idaho, contain large quantities of euxenite and columbite and constitute an important strategic reserve. Low-grade columbium resources are known in the titanium and aluminum ores of Arkansas, which offer additional emergency sources of columbium.

GOVERNMENT PROGRAMS

All stockpile objectives have been exceeded. The stockpile totals are supplmented by more than 15 million pounds of contained pentoxides in concentrates bought under a special Government purchase program and by columbium oxide and ferrocolumbium purchased under individual contracts.

The increased demand during World War II for ferrocolumbium and dependence on waterborne imports resulted in control of columbite imports and allocation controls on ferrocolumbium. During the Korean action, controls were again applied on the production, distribution, and use of ferrocolumbium and ferrotantalum-columbium. Controls on the purchase and use of columbium are not now in effect.

Government support for columbium continues to be offered by the Office of Minerals Exploration (OME) which encourages exploration for columbium ores in the United States by providing loans for 50 percent of approved costs of exploration.

Financial support of columbium research is supplied by various Government agencies (Navy, Air Force, NASA, AEC) to universities, industries, and private research organizations.

PRICES

During 1963, prices for columbite ore, c.i.f. U.S. ports, were quoted by E&MJ Metal and Mineral Markets at \$0.90 to \$1.00 per pound of contained pentoxides for material having a Cb_2O_5 to Ta_2O_5 ratio of 10 : 1, and \$0.80 to \$0.90 for that having an 8.5 : 1 ratio.

In 1963, columbium metal, reported by E&MJ Metal and Mineral Markets was quoted at \$36 to \$50 per pound depending upon form (roundels, electrode segments, and ingot) and quantity.

The price of ferrocolumbium during most of 1963 was \$3.45 per pound of contained columbium (50 to 60 percent columbium). In mid-December the price dropped to \$3.00 per pound. The price of ferrotantalum-columbium was \$3.05 per pound of contained columbium plus tantalum.

TAXES

Depletion allowance is 23 percent for domestic producers of columbium ore, and 15 percent for U.S. producers with production in foreign countries.

TRANSPORTATION AND STORAGE

Transportation and storage of columbium ores or concentrates present no special problems. For stockpiling, they are packed in 55-gallon galvanized steel drums, but commercial shipments also are made in cotton or burlap bags and wooden kegs.

Columbium powder and pellets are usually packed in polyethylene bags in steel drums to prevent contamination by dust and iron.

Columbium fluoride is soluble in water and will hydrolyze to evolve hydrofluoric acid. The containers must be kept dry at all times to prevent production of the highly corrosive acid fumes. Satisfactory containers include rubber-lined drums or coated fiber containers. The storage area for the fluoride should be dry, cool, ventilated, and fireproof without a sprinkler system.

RESEARCH

Research on columbium technology has greatly accelerated in the past 15 years (*15*). Industry, private research institutions, universities, and Government agencies have published information on the ore resources, properties, perparation, and uses of the metals, their alloys, and their compounds.

The Bureau of Mines has been evaluating resources (*13*) and has been studying analytical procedures (*6, 18*), extraction, separation, reduction, and purification of the metal (*5, 7, 9, 14*), and development of alloys (*1, 2, 20*) in re-

cent years. Facets of Bureau work have included sampling and evaluation of the Bear Valley Placers in Idaho and other northwestern placers, determination of columbium reserves in Arkansas and the development of methods to concentrate the minerals and extract the metal, benefication studies of columbium-tantalum bearing minerals in alluvial black-sand deposits in the Northwest, extraction of columbium and tantalum from low-grade ores, including euxenite and tin slags, separation by solvent extraction, anhydrous separation, reduction techniques, and preparation of high-purity metals and alloys.

Industry and institutions have numerous research programs under way. These include new uses, high-purity metal production, improved high-temperature alloys, processes for concentrating pyrochlore-type ores, improved impact- and corrosion-resistant steels, and other basic problems.

Important recent results of research have included new commercial separation methods, new techniques to produce ingot by electron bombardment, and improved alloys.

In addition to studies being conducted by the Bureau of Mines, research on the development of columbium-base alloys for use at elevated temperatures is currently being sponsored by the U.S. Atomic Energy Commission (AEC), the National Aeronautics and Space Administration (NASA), and the U.S. Department of Defense (*10, 12, 22*). Studies sponsored by the Navy, Air Force, and NASA are investigating protective coatings which will prevent or retard oxidation at the elevated temperatures encountered by space and aeronautical structures (*3, 8, 11, 21, 23*).

OUTLOOK

Despite competition between columbium and substitute materials, the consumption of columbium as indicated by current trends should continue to grow. Columbium consumed as an alloying material in steel will represent the largest volume usage. Because of its excellent corrosion-resistant properties, columbium will be used in increasing amounts in high-temperature stainless steels and in oil and gas transmission pipes. Columbium steels also will be used in the chemical-processing industry, construction machinery, and aircraft landing gear because of the corrosion-, heat-, and impact-resistant properties of columbium alloys.

Columbium metal and nonferrous columbium-base alloys having exceptional high-temperature properties are finding new and specialized applications in nuclear power reactors, experimental breeder reactors, gas turbines, jet engines, and missile and aircraft structures. The demand for columbium in these specialized areas should accelerate rapidly and represent the largest single area of growth. Columbium-base alloys, which resist both the elevated temperatures encountered during reentry and the low temperatures in outer space, are being considered as structural materials for space capsules.

Because of their superconducting characteristics at cryogenic temperatures certain columbium-base alloys will develop an additional economically significant market. Superconducting alloys and compounds of columbium probably will be used to control and contain nuclear fusion reactions. The extremely high temperatures of fusion reactions exceed the melting points of all known materials and must be contained by a magnetic force; superconducting columbium alloys produce a containing magnetic field without requiring the continued addition of electrical energy.

Although low-grade domestic sources of columbium have been discovered in both pyrochlore and columbite-tantalite ore deposits, the domestic industry will continue to draw upon imports for most of its supply of raw material.

PROBLEMS

The major potential problem facing the domestic columbium industry has been that of supply. However, with the development of pyrochlore deposits in Canada the United States will not be as dependent upon less reliable sources as in previous years.

Because of the complex nature of columbium-bearing ores, efficient separation and recovery are both expensive and difficult. The development of economical extraction processes is another major problem facing the columbium industry. Recent research has led to the use of such complex practices as fractional distillation, solvent extraction, and fractional crystallization to separate columbium from low-grade columbium-tantalum ores. Although scientifically practical, these operations involve costly equipment and reagents and are too expensive to be used commercially. When current sources of economic supply become depleted and the price justifies their use, some of the newer extraction techniques will be utilized.

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COPPER

By F. L. Wideman [1]

COPPER has been essential to mankind's existence from prehistoric times to the present. Its value from antiquity until the 19th century was related to its malleability and ease of working, its attractive colors in alloys and unalloyed forms, its durability and corrosion resistance, and its availability. The first uses were for utensils, tools, and weapons and later uses included pipe, statuary, objects of art, and building and architectural uses where permanence and beauty were essential qualifications. These uses of copper have grown tremendously and its ability to form numerous alloys has led to a myriad of applications from minature eyelets to huge bronze battleship propellers. The 19th century marked the beginning of an epoch of copper's greatest use in the generation and transmission of electrical energy. The conductivity of copper was fundamental to the spectacular growth of the electrical industry and all associated industries relying on electricity for light, power, and heat. More than half the copper produced is used for the transmission of electricity.

The United States has been the largest copper-producing nation in the world since 1883, except for 1934 when economic conditions adversely affected domestic production and Chile ranked first. Ore and waste produced at copper mines in the United States in 1960–63 was more than the total materials handled at mines producing ore of any other metal. Four large companies mine, smelt, and refine a large percentage of the domestic production; and plants associated with these companies account for more than half the output of fabricated products.

Outside the United States, two American companies operate the large mines of Chile and one of these companies operates the largest mine in Peru. Output of Northern Rhodesia is derived from six mines operated by two companies and total production from the Republic of the Congo is derived from several mines controlled by one company. A large percentage of the production from Canada came from six large mines in Quebec and Ontario and two mines in Manitoba-Saskatchewan.

There are many copper minerals but only a few are important commercially. Copper ores occur in many types of deposits in various kinds of host rocks. Porphyry deposits, however, contain most of the world's reserves and are adaptable to mining by open-pit or block-caving methods. Cut and fill, shrinkage stoping, and room and pillar are large-scale methods used in underground mining. Copper metal is recovered from its sulfide ores by concentrating, smelting, and refining and by leaching followed by precipitation or electrowinning for oxide ores. Recently, encouraging results have been obtained in treating refractory ores such as the silicates. The method used to refine copper depends to a large extent on the nature of the byproducts and impurities present. Blister copper containing precious metals, tellurium, and selenium is electrolytically refined and copper containing volatile impurities can be fire refined. The final refined product is almost pure (99.9+ percent) and is cast in several refinery shapes which are used to produce fabricated and semifabricated copper and copper-base alloy products. Metals recovered as byproducts from the treatment of copper ores include iron, lead, zinc, nickel, cobalt, gold, silver, platinum-group metals, selenium, tellurium, and arsenic. Sulfur is also recovered in byproduct sulfuric acid.

Aluminum serves as an alternate metal for copper and its alloys in many electrical, structural, and decorative applications. Copper-clad metals, stainless steel, and plastics also have replaced copper in some uses.

The copper industry has been able to meet an ever-increasing demand by the discovery of new resources and advances in technologies which have converted uneconomic and low-grade material into ore. The world reserve, in terms of metal copper, was estimated to be 212 million tons in 1960, almost double the reserve in 1935. Six principal areas contain 85 percent of the measured and indicated reserve of the world.

[1] Commodity specialist.

In order of the magnitude of reserves these are: the western slope of the Andes in South America, the central African copper belt in Northern Rhodesia and Congo (Léopoldville), the Western United States, the Ural Mountains and the Kazakstan regions in the U.S.S.R., the Precambrian area of central Canada, and the Lake Superior region of North America.

Copper products in use that eventually will be discarded as scrap are another reserve being accumulated principally in industrial countries of the world. In the United States this resource, estimated to be more than 35 million tons, provides about one-fourth the annual supply.

Mining and metallurgical research has made immense quantities of low-grade ore available which otherwise would have been of no value as a source of copper. One of the most effective conservation practices is the reclamation of copper from scrap and another noteworthy practice is the recovery of copper by leaching low-grade material unsuited to concentration.

In the past 5 years strong demand and high prices, comparatively free from fluctuations, encouraged increased world mine production from new mines and accelerated rates at established mines. A new record for world production of 5.2 million tons was established in 1963. Although the United States remains as the largest producer of copper, its percentage of world production has declined from about 52 percent in 1926 to 23 percent in 1963. Chile, which had usually ranked in second place, was surpassed by Northern Rhodesia in 1953, 1954, 1960, and 1961. Estimated production of the U.S.S.R. placed it in second place in 1962 and 1963. Mine productivity capacity in the United States has increased about 12 percent since World War I. However, mine productivity in terms of output of copper per man-hour has increased more than sixfold.

The United States continued to be the largest copper consuming country in the world accounting for 30 percent of the world total. Since World War II, about half of the domestic consumption has been supplied by U.S. mine production, and one-fourth each by copper recovered from secondary materials and by imports. From 1959 through 1963, Chile supplied 44 percent of the imports of unmanufactured material; Canada 19 percent; Peru 15 percent; and the Republic of South Africa 6 percent.

Average annual prices in the United States have ranged from 5.67 cents per pound in 1932 to a peak of 41.88 cents per pound in 1956 (the high of 46 cents was reached in July 1956). The price of copper declined to 29 cents per pound in early 1961. Producers began curtailments of mine production and prices rose to 31 cents by May 1961 and producers' prices remained at that price through 1963, the longest period of price stability except when under Government control.

There is a rising trend in world consumption caused by expanding electrification, increased use of copper by the construction industry, and efforts to accelerate progress in developing nations. Appraising the future of the copper industry on the basis of past and current activities, there will be adequate sources of ore, ample processing equipment and copper should keep its share of the market for metals. The copper industry is confronted with technical and economic problems related to mining, processing, uses, and prices. Although there is ample reserve of ore for the domestic industry for some years, a fundamental problem is the assurance of a continuing supply at prices competitive to aluminum and other substitute materials.

BACKGROUND

Copper and gold were undoubtedly the first metals discovered and used by man. They are often found in the native state, are bright, pleasing in appearance, and easily worked. Industrially, however, copper was used first because when beaten it hardens sufficiently to permit primitive man to fashion utensils and sharp implements and weapons of lasting quality. Gold, which is soft, was used principally for ornamentation. The earliest history of copper is obscure, some theories have been advanced that its discovery was associated with Neolithic civilizations of the late stone age. Artifacts of hammered copper have been found among Chaldean remains that date back to 4500 B.C. and objects of copper that may be even more ancient have been excavated from Badarian graves in the Fayum of Egypt. Some writers believe that at least 20 centuries separated the first use of hammered copper and the beginning of copper smelting about 3800 B.C. This dates the discovery of copper circa 6000 B.C.

Little is known about prehistoric mining of copper although it seems certain that open-pit and underground mining methods were used. Diversity of opinion exists on the origin of smelting, but it is generally thought that the process first began about 3500 B.C. in Elam, an ancient country northeast of the valleys of

the Euphrates and Tigris Rivers. The most important deposits were in the eastern Mediterranean area, the Near East, central Asia, and Europe. It is thought that the copper used in southern Mesopotania (3500–3000 B.C.) came from deposits in Asia Minor that contain the same impurities that are present in the copper relics. These deposits also supplied the Assyrians much later and peaks of production from the area were between 2400–2000 B.C. and 1500–1200 B.C.

Definite records have been found that describe mining in the Sinai Peninsula about 3800 B.C. and the discovery of crucibles near the mines indicates that the early extraction of metal included some refining. Copper was produced in Egypt from Dynasty III (2600 B.C.) onward. It has been estimated that 10,000 tons of copper were produced in Egypt in 1,500 years. Egypt became dependent on imports of copper from Cyprus and Armenia in the 12th century. Copper mining in Cyprus began about 2500 B.C. and was successively under the dominion of Egyptians, Assyrians, Phoenicians, Greeks, Persians, and Romans. The same deposit is still being exploited and produced 29,000 tons in 1963.

Copper was used in China as early as 2500 B.C. and bronze castings were made about 2250 B.C. No mention of the source of copper is made in the epic of Shu King but it is traditional in China that metal came from the West. This is substantiated by the known existence of two trade routes to China, which traversed copper-producing areas, one by way of Altai and Lake Balkhash in Siberia and the other by Tarim and Turkestan.

In Europe, copper mines in Austria, Germany, France, Spain, Greece, and Tyrol were worked in the bronze age. Mines in Mitterberg in Tyrol probably were worked from about 1600 B.C. to the Hallstatt period in the iron age, about 800 B.C. Probably the most important copper deposits in Europe were those of Spain and Portugal, including the remarkable Rio Tinto ore body which is still being exploited. It is believed that the Phoenicians were acquainted with the mineral deposits of Britain as early as 1500 B.C. The Romans mined copper extensively in several parts of Britain, notably in Anglesey, Cumberland, and North Wales. It is probable that much of the metal was exported, one cake found near Llandudno was stamped "Scio Roma"—"to my partner in Rome."

Evidence of the first use of copper in North America was discovered by archeologists in pits on the Upper Peninsula of Michigan and on Isle Royale in Lake Superior. It has been estimated that there are thousands of pits on Isle Royale alone. The pits were excavated in mining and followed deposits of native copper from surface outcrops. A section of charred log found in one pit and subjected to carbon-dating methods was determined to be approximately 3,000 years old. Another piece from the same pit was tested and found to be about 3,800 years old. Working copper in the Americas seems to have stopped with the cessation of these operations about 1000 B.C. and was not resumed until A.D. 100–200 elsewhere on the continents. Copper was first produced in the American Colonies at Simsbury, Conn., in 1709 and a significant ore body was found in Orange County, Vt. (Ely mine), in 1820. It is not known whether or not any prehistoric race used copper from deposits in the Southwest, but it is reported that a Spanish officer in charge of a military post was shown croppings of native copper near Silver City, N. Mex., in 1800. Discovery of the ore deposits of Michigan in the early 1840's began a new era for copper production in the United States. Extensive ore bodies were found in Montana and Arizona during 1860–80 and smelter production from domestic ores increased from 728 tons in 1850 to 30,240 tons in 1880. In Bingham Canyon, Utah, the Utah Copper Co., later absorbed by the Kennecott Copper Corp., began exploitation of a large low-grade porphyry deposit in 1906. The success of this operation stimulated search for and development of other large deposits of similar characteristics, both in the United States and abroad. Development of the froth flotation process in the first two decades of the 20th century vastly increased the availability of copper contained in the large low-grade deposits which constitute most of the copper reserves.

The copper industry of Chile and Peru is an ancient one. It is known that aborigines worked some of the deposits before the arrival of the conquistadores. The Spaniards were more interested in gold than other metals and did nothing with the copper deposits until the beginning of the 17th century. The high-grade oxide and carbonate ores were worked in a primitive way for many years after. Chile ranked third as a world producer from 1801 to 1850 and was the largest producer in the world from 1851 to 1880. Production rapidly declined thereafter until the decade 1921–30 when Chile became the second largest producer, a position it has held almost consistently since.

When copper was mined first in central Africa is not known. Portugese explorers noted the production of copper and iron in Katanga in their 18th century reports. Ore bodies in the Katanga, Northern Rhodesia, and Trans-

vaal had been mined extensively and crosses of copper were items of commerce. Europeans arriving in the late 19th and early 20th centuries were shown outcrops of ore and ancient copper mines by Africans, resulting in the exploration and development of one of the most productive areas of the world.

SIZE AND ORGANIZATION OF THE INDUSTRY

The value of the copper content of ores produced in the United States in 1961 through 1963 exceeded that of the ore of any other metal except iron and averaged more than $734 million in the 3 years. Ore and waste handled at copper mines was more than the total material handled at mines of any other metal in 1960 through 1963 and averaged 394 million tons for the 4 years. The United States has been the largest copper-producing country in the world since 1883, except for 1934 when economic conditions adversely affected domestic production and Chile ranked first. The United States produced 23 percent of the world mine production in 1963. In that year, smelters in the United States produced 23 percent of the total world smelter production from domestic ore and an additional 1 percent from imported ore. Other principal copper-producing nations were the U.S.S.R., Chile, Northern Rhodesia, Canada, and the Republic of the Congo, in that order.

The primary copper industry in the United States is composed of approximately 200 companies engaged in the production and sale of copper. However, about a dozen companies produced more than 95 percent of the output. The major firms are vertically integrated and have mining, smelting, refining, fabricating facilities, and marketing organizations. Other large producers mine and process through the smelting or refining stage and many companies mine and concentrate their ore and ship the product to custom plants for smelting and refining.

In 1963, 25 mines accounted for 97 percent of the domestic output; the 5 largest produced 47 percent, and the 10 leading mines supplied 72 percent. Three companies, Kennecott Copper Corp., Phelps Dodge Corp., and The Anaconda Company usually account for about two-thirds of the annual domestic mine production. Kennecott and Phelps Dodge are the largest producers and supply about 31 percent and 21 percent, respectively, of each years total. The principal mining companies in the United States in 1963 were:

Company	Recoverable copper content of ore mined (short tons)	Percent of U.S. total
Kennecott Copper Corp	382,000	31
Phelps Dodge Corp	260,000	21
The Anaconda Company	121,000	10
Magma Copper Co	103,000	8
American Smelting and Refining Company	72,000	6
White Pine Copper Co	57,000	5
Inspiration Consolidated Copper Co	57,000	5
Tennessee Corp	33,000	3
Duval Corp	23,000	2
Total above companies	1,108,000	91
Total United States	1,213,000	100

Copper smelting capacity in the United States (exclusive of lake smelters in Michigan) totaled approximately 8.4 million tons of charge. The smelter of Phelps Dodge Refining Corp., at Laurel Hill, N.Y., was closed and dismantled in 1963 reducing the total charge by about 200,000 tons. Four companies control about 87 percent of the capacity. Copper smelting companies and their approximate percentage of the total U.S. smelting capacity are:

Company	Percent of total capacity (charge)
Phelps Dodge Corp. and Phelps Dodge Refining Corp	30
Kennecott Copper Corp	29
American Smelting and Refining Company	16
The Anaconda Company	12
Inspiration Consolidated Copper Co	4
San Manuel Copper Corp	4
American Metal Climax, Inc	2
Magma Copper Co	2
Tennessee Copper Co	1
Total	100

Lake smelter capacity in 1963 totaled 177,000 tons, as follows:

	Short tons
Calumet & Hecla, Inc	100,000
White Pine Copper Co	65,000
Quincy Mining Co	12,000

Tank capacities at electrolytic copper refineries in the United States in 1963 was about 1,964,000 tons. Three companies account for about 68 percent of total output. Refining companies and their approximate percentages of the U.S. electrolytic refinery capacity in 1963 are:

Company	Percent of total U.S. capacity
American Smelting and Refining Company	24
Phelps Dodge Refining Corp	23
Kennecott Copper Corp	21
International Smelting & Refining Co.[1]	12
American Metal Climax, Inc	8
The Anaconda Company	8
Inspiration Consolidated Copper Co.[2]	2
Lewis Mathes Co., Division of Cerro Corp	2
Total	100

[1] A subsidiary of The Anaconda Company.
[2] 28 percent controlled by The Anaconda Company.

Lake and fire refining capacities in the United States totaled 371,000 tons in 1963 or about 16 percent of the Nation's refinery capacity. Refining companies and their approximate percentage of the U.S. Lake and fire refining capacity are:

Company	Percent of total U.S. capacity
American Metal Climax, Inc	34
Kennecott Copper Corp	23
White Pine Copper Co	17
Calumet & Hecla, Inc	16
Phelps Dodge Refining Corp	7
Quincy Mining Co	3
Total	100

Fabricating establishments are the principal consumers of refined copper. They work the metal into semifinished forms such as sheet, strip, rod, tube, wire, and extruded and rolled shapes which are the raw materials for a vast industry which manufactures articles for final consumption or parts for products of other industries. About 35 companies are the important users of raw copper and are, for the most part, wire and brass mills. The larger fabricators, representing more than 50 percent of the total volume of business, are affiliated with the major copper producers, as follows:

Fabricating company	Associated with—
Chase Brass & Copper Co, Inc	Kennecott Copper Corp.
The Okonite Co	Do.
The Anaconda American Brass Co	The Anaconda Company.
Anaconda Wire & Cable Co	Do.
Phelps Dodge Copper Products Corp	Phelps Dodge Corp.
Calumet & Hecla, Inc.—Wolverine Tube Division	Calumet & Hecla, Inc.
C. G. Hussey & Co., Division of Copper Range Co	Copper Range Co.
New Haven Copper Co	Tennessee Corp.
Cerro Copper & Brass Co., Division of Cerro Corp	Cerro Corp.
Circle Wire & Cable Co	Do.

American Smelting and Refining Company has substantial stock interests in General Cable Corp. (31.7 percent) and Revere Copper & Brass Corp., Inc. (35 percent).

The more important fabricators not affiliated with the copper producers are:

Brass mills

Bohn Aluminum & Brass Corp.
Bridgeport Brass Co., Division of National Distillers & Chemical Corp.
The Bristol Brass Corp.
Chicago Extruded Metals Co.
Detroit Gasket & Manufacturing Co.
The Electric Materials Co.
Halstead Metal Products
International Silver Co.
Mueller Brass Co.
Olin Mathieson Chemical Corp.
Reading Tube Co., Division Progress Manufacturing Co.
Scovill Manufacturing Co.
Triangle Conduit & Cable Co., Inc.
U.S. Mint Services
Volco Brass & Copper Co.
Western Electric Co., Inc.

Wire mills

Copperweld Steel Co.
General Cable Corp.
Hatfield Wire & Cable Division, Continental Copper & Steel Industries, Inc.
Narragansett Wire Co.
Rods, Inc.
Rome Cable Corp.
Triangle Conduit & Cable Co., Inc.
Western Electric Co., Inc.

Following is a list of the principal secondary copper smelters in the United States in 1963:

Barth Smelting & Refining Co.
Benjamin Harris & Co.
W. J. Bullock, Inc.
Colonial Metals Co.
Elesco Smelting Corp.
Federal Metal Co.
Federated Metals Division (American Smelting and Refining Company)
George A. Avril Smelting Corp.
H. Kramer & Co. (include Ajax Metal Division)
I. Schumann & Co.
Interstate Smelting & Refining Co.
Liberman & Gittlen Metal Co., Inc.
Nassau Smelting & Refining Co.
North American Smelting Co.
R. Lavin & Sons, Inc.
River Smelting & Refining Co.
Roessing Bronze Co.
North Chicago Refiners & Smelters, Inc.
Northwestern Metal Co.

GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Copper is widely distributed in nature. The earth's crust is estimated to contain an average of 70 parts per million. However, there are relatively few large copper-producing areas in the world despite its wide distribution. Many countries have some copper ore deposits; 8 countries each mined more than 100,000 tons of recoverable copper in 1963, 18 produced more

780-887 O—65——18

than 10,000 tons; and about 20 other nations recorded some output.

Most of the copper mined in the United States is produced in five Western States (91 percent in 1963) and approximately 85 percent of the remainder is obtained from Michigan and Tennessee. Most of the production in Chile comes from three large mines and the remainder comes from a number of small- and medium-size mines. Production from Peru is derived principally from two mines. Output in Congo (Léopoldville) comes from properties of one company and copper from Northern Rhodesia is produced from six large mines. Ontario and Quebec combined produced more than 70 percent of Canada's output but there has been a sharp upturn in production from British Columbia in the past few years. Estimates of production from the U.S.S.R. are usually included with data for Europe, although the production comes from the widely separated areas of Kazakstan, Uzbekistan, the Urals, Transcaucasia, West Siberia, and the Kola Peninsula. Yugoslavia recently became the second largest producer in Europe. Plans for development of extensive deposits in western Poland have been reported.

Concentrating and smelting facilities usually are situated near the principal mines and some process ore from smaller producers. There are eight primary smelters in Arizona, three in Michigan, and one each in Utah, Montana, Nevada, New Mexico, Tennessee, Texas, New Jersey, and Washington. The latter two smelters are at seaports. Of the smelters in Canada, three are in Ontario, two in Quebec and one in Manitoba. Mexico has two operating smelters and another is idle. Six smelters in Chile and two in Peru constitute the smelting industry in South America.

The Federal Republic of Germany has four smelters; Belgium and Sweden two; and Finland, Norway, Spain, and Yugoslavia each have one. Copper smelting is an important industry in Japan where eight companies operate several plants. A smelter operates in India and two in Turkey treat copper materials. The largest copper smelter in the world is in Northern Rhodesia where there are two others. One company has three smelters in the Republic of the Congo. Elsewhere, in Africa there are two operating smelters and one under construction in the Republic of South Africa, one each in Southern Rhodesia, South-West Africa, and Uganda. There are three smelters in Australia and one in Tasmania.

About 59 percent of the domestic electrolytic refining capacity and 61 percent of the output is accounted for in six refineries on the Atlantic coast in New York City, Carteret and Perth Amboy, N.J., and Baltimore, Md.; one each in Arizona, Missouri, Montana, Texas, Utah, and Washington supply the remainder. Three Michigan plants produce Lake copper and refineries in Maryland, New Jersey, New Mexico, and Texas produce fire-refined copper.

For many years before World War II, refining and smelting capacity in the United States exceeded the supply of domestic materials, and the excess capacity was used for the treatment of foreign crude material. Since the war, foreign producers have made great progress in building their own reduction works.

There are two electrolytic refineries of large capacity in Canada and one of small capacity in Mexico. Four establishments in Chile and one in Peru produce electrolytic copper. Numerous plants refine imported or domestic copper materials in Austria, Belgium, Finland, France, Federal Republic of Germany, Norway, Spain, Sweden, the United Kingdom, and Yugoslavia. In Africa, there are two refineries in the Republic of the Congo, four in Northern Rhodesia, and one each in the Republic of South Africa and Southern Rhodesia. Facilities of seven companies in Japan have an aggregate capacity of about 385,000 short tons. India and Korea each have a refinery, and Turkey has an electrolytic plant of small capacity and two fire refineries, only one of which is active. Two refineries in Australia and one in Tasmania have a total capacity in excess of a quarter million tons.

Although there are 20 fabricating plants in the New England States, most of the major establishments of the United States are in the Connecticut Valley area. Mid-Atlantic States have 26 plants; North-Central States 20; Southern States 1; and California 3.

The fabricating industry of Canada is situated in the provinces of Montreal, Quebec, and Ontario. Primary copper consumed in the manufacture of semifabricated products totaled 156,000 tons in 1962. The fabricating industry in Chile is small and production in 1961–63 averaged about 4,000 tons.

The fabricating industry of Europe, located in 16 nations excluding Soviet bloc nations, is large and uses approximately 2,150,000 tons of refined copper a year (the use of scrap and scrap alloys is excluded). It has been estimated that about 1,000,000 tons of refined copper is consumed in Soviet sphere countries.

Production of semimanufactures of selected European Nations in 1963 was as follows:

Country	Short tons
Austria	44,700
Belgium	136,900
France	392,300
West Germany	673,700
Italy	356,000
Denmark, Finland, Norway, Sweden	217,500
Switzerland	71,600
Spain	69,900
United Kingdom	795,200

Japan, the only other nation not in the Soviet sphere, having a large fabricating industry produces more than 620,000 tons of semifabricated products annually. India produces about 3,400 tons of the materials, slightly more than half of which are brass and bronze semimanufacturers.

Collection, preparation, and treatment of secondary materials is widespread. The collection of scrap is carried on in almost every community and in many, there are dealers that sort, bale, and otherwise prepare the scrap for sale and shipment to establishments that use it. These are primary and secondary smelters, ingot makers, brass mills, chemical plants, and other consumers. However, the principal source of unalloyed and alloyed copper scrap is in the heavily populated industrial areas and most of the plants that treat secondary materials are located near them. There are 60 secondary smelters in 21 States that treat scrap in addition to the brass and wire mills listed previously.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Commercial copper is classified broadly by the method by which it is refined. Thus copper is described as electrolytic or fire refined. There are three basic classes of commercial copper that arise from the high affinity of molten copper for oxygen, and the methods employed for its control. They are designated as tough-pitch copper, oxygen-free copper, and deoxidized copper.

Electrolytic copper is that refined by electrolytic deposition. *Fire-refined copper* is refined by using a furnace process only. *Tough-pitch copper* is electrolytic or fire-refined copper cast in refinery shapes and containing a controlled quantity of oxygen in cuprous oxide. *Oxygen-free copper* is refined copper cast under a deoxidizing atmosphere that eliminates all cuprous oxide without using metallic or metalloidal deoxidizers. *Deoxidized copper* is refined copper freed from cuprous oxide through use of metallic or metalloidal deoxidizers. The terms "electrolytic" and "fire refined," when used alone, usually refer to either electrolytic or fire-refined tough-pitch copper without elements other than oxygen present in significant quantities. The five major classifications are applicable, through extension, to fabricator products made therefrom.

Resistivity is used instead of conductivity in designations of grades of copper. The value of 0.15328 ohm-gram/meter^2 is the International Annealed Copper Standard (IACS) for resistivity equal to 100 percent conductivity.

High conductivity copper has a minimum conductivity of 100 percent IACS in the annealed condition. *Casting copper* is fire-refined tough-pitch copper, usually derived from secondary metal and cast into ingot and ingot bars only for use in making foundry castings, but no wrought products. *Phosphorized copper* is a general term applied to copper deoxidized with phosphorus. It is the most commonly used deoxidized copper. *Arsenical copper*, *phosphorus-bearing copper*, *silver-bearing copper*, *tellurium-bearing copper* contain the designated element in amounts agreed upon between the supplier and the consumer. Any of these alloyed coppers can be produced as tough-pitch, oxygen-free, or deoxidized varieties.

Several types of each class of commercial copper are available in refinery shapes, and wrought and cast products. Eighteen such types are recognized by the American Society for Testing Materials in its Classification of Coppers. Refinery shapes and fabricators' products, currently produced in commercial forms, are listed in table 1.

Several refinery shapes are made depending partly on the end use of the copper.

Wire bar is a refinery shape for rolling into rod (and subsequent drawing into wire), strip, or shape. Wire bars are approximately 3½ to 5 inches square in cross section, usually from 38 to 54 inches in length, and weighing from 135 to 420 pounds. They are tapered at both ends when used for rolling into rod for subsequent wire drawing and may be unpointed when used for rolling into strip. Cake is used for rolling into plate, sheet, strip, or shape. It is rectangular in cross section of various sizes and ranges from 140 to 4,000 pounds or more in weight. Billet is the refinery shape used primarily for tube manufacture. It is circular in cross section, usually 3 to 10 inches in diameter and in lengths up to 52 inches; weight from 100 to 1,500 pounds. Ingots and ingot bars are employed for alloy production (not fabrication). Ingots usually weigh from 20 to 35 pounds and ingot bars from 50 to 70 pounds. Both usually are notched to facilitate breaking into smaller pieces and are used for remelting. Unmelted flat plate produced by electrolytic refining is called cathode. The customary size is about 3 feet square and about ½ to ⅞ inches thick, weighing up to 280 pounds.

TABLE 1.—*Classification of coppers*

Designation	Type of copper	Forms in which available							
		From refiners				From fabricators			
		Wire bars	Billets	Cakes	Ingots and ingot bars	Flat products	Pipe and tube	Rod and wire	Shapes
Cath	Electrolytic cathode	Available in cathodes only.							
		Tough pitch coppers							
ETP	Electrolytic tough pitch	X	X	X	X	X	X	X	X
FRHC	Fire-refined high conductivity tough pitch	X	X	X	X	X	X	X	X
FRTP	Fire-refined tough pitch		X	X	X	X	X		X
ATP	Arsenical tough pitch		X	X		X	X	X	
STP	Silver bearing tough pitch	X	X	X	X	X	X	X	X
SATP	Silver bearing arsenical tough pitch		X	X		X	X		
CAST	Casting				X				
		Oxygen-free coppers							
OF	Oxygen-free without residual deoxidants	X	X	X		X	X	X	X
OFP	Oxygen-free, phosphorus bearing	X	X	X		X	X	X	
OFPTE	Oxygen-free, phosphorus and tellurium bearing.		X					X	X
OFS	Oxygen-free, silver bearing	X	X	X		X		X	X
OFTE	Oxygen-free, tellurium bearing		X					X	X
		Deoxidized coppers							
DHP	Phosphorized, high residual phosphorus	X	X	X		X	X	X	X
DLP	Phosphorized, low residual phosphorus		X	X		X	X	X	X
DPS	Phosphorized, silver bearing		X	X		X	X		X
DPA	Phosphorized, arsenical		X			X	X		
DPTE	Phosphorized, tellurium bearing		X					X	X

Definitions of fabricators' copper products follow:

Wire, a solid section including rectangular flat wire but excluding other flat products, furnished in coils or on spools, reels, or bucks. Flat wire may also be furnished in straight lengths.

Tube, a hollow product of round or any other cross section, having a continuous periphery.

Pipe, seamless tube conforming to the particular dimensions, commercially known as Standard Pipe Sizes.

Shape, a solid section, other than rectangular, square or standard rod, and wire sections, furnished in straight lengths. Shapes are usually made by extrusion, but may also be fabricated by drawing.

Flat product, a rectangular or square solid section of relatively great length in proportion to thickness. Included in the designation flat product depending on the width and thickness, are plate, sheet, strip, and bar. Also included is the product known as flat wire.

Rod, a round, hexagonal, or octagonal solid section. Round rod for further processing into wire (known as hot rolled rod, wire-rod, or redraw wire) is furnished coiled. Rod for other uses is furnished in straight lengths.

Copper powder, finely divided copper particles produced by (1) high velocity atomization of molten copper with streams of compressed gas, steam, or water; (2) gaseous reduction of finely divided oxides; and (3) precipitation from solutions.

The various types of copper are graded by the American Society for Testing Materials (ASTM) principally according to their chemical composition and electrical resistivity. Specifications adopted for these coppers are as follows:

B4–42 Lake copper wire bars, cakes, slabs, billets, ingots, and ingot bars (must originate on the Northern Peninsula of Michigan).

(a) Low-resistance Lake copper—minimum purity of 99.900 percent, silver being counted as copper.

	Resistivity, maximum, international ohm-gram/meter[2]
Wire bars	0.15328
Cakes, slabs, and billets:	
For electrical use	.15328
For other uses	.15694
Ingots and ingot bars	.15694

(b) High resistance Lake copper—minimum purity of 99.900 percent, silver and arsenic being counted as copper; resistivity greater than 0.15694 international ohm-gram/meter[2] at 20°C.

B5–43 Electrolytic copper wire bars, cakes, slabs, billets, ingots, and ingot bars—minimum purity 99.900 percent, silver being counted as copper.

	Resistivity, maximum, international ohm-gram/meter[2]
Wire bars	0.15328
Cakes, slabs, and billets:	
For electrical use	.15328
For other uses	.15694
Ingots and ingot bars	.15694

B115–43 Electrolytic cathode copper—minimum purity of 99.90 percent, silver being counted as copper. The copper shall have a resistivity not to exceed 0.15328 ohm-gram/meter[2] at 20°C (annealed).

B170–59 Oxygen-free electrolytic copper wire, bars, billets, and cakes—minimum purity of 99.95 percent, silver being counted as copper. Resistivity not to exceed 0.15328 ohm-gram/meter[2] at 20°C (annealed). Test samples shall be free from cuprous oxide as determined by microscopic examination at 75 X magnification. Prepared wire samples, annealed at 800° to 875°C for 20 minutes in hydrogen, shall withstand four 90° bends (2 each in opposite directions) without fracture.

B72–60 Fire-refined casting copper—must conform to the following requirements as to chemical composition:

	Grade A percent	*Grade B percent*
Copper plus silver, minimum	99.75	99.50
Arsenic, maximum	.0075	.10
Antimony, maximum	.012	.012
Bismuth, maximum	.003	.003
Iron, maximum	.010	.010
Lead, maximum	.100	.30
Nickel, maximum	.10	.10
Oxygen, maximum	.10	.10
Selenium, maximum	.040	.040
Sulfur, maximum	.01	.01
Tellurium, maximum	.014	.014
Tin, maximum	.025	.05

B216–49 Fire-refined copper for wrought products and alloys—must conform to the following requirements as to chemical composition. (No resistivity specifications.)

	Percent
Copper plus silver, minimum	99.88
Arsenic, maximum	.012
Antimony, maximum	.003
Selenium plus tellurium, maximum	.025
Nickel, maximum	.05
Bismuth, maximum	.003
Lead, maximum	.004

Copper-Base Alloy Terms

Copper and copper-base alloys comprise a series of metals that include all the alloys which are at least 40 percent copper and where the amount of copper is not less than the amount of any other constituent. There are essentially four well-known copper-base alloys—brass, bronze, nickel-silver, and cupro-nickel. Modern nomenclature for certain compositions departs from the original concept that brasses are copper-zinc alloys and bronzes principally copper and tin. Metallurgical research has developed important new alloys and necessitated revision of many original, simple definitions.

Brass may be defined as any copper-base alloy containing zinc as the principal alloying constituent, with or without smaller quantities of other elements. Some of the alloys known as nickel-silver could be termed "brasses," but these alloys also possess enough distinctive qualities to warrant separate classification. There are alloys that are definitely brasses by definition, yet have names that include the word "bronze;" for example, *commercial bronze* containing 90 percent copper and 10 percent zinc.

The term *bronze* is seldom used alone and the copper-tin alloys have come to be known as *phosphor bronze* because of the small residual phosphorus content. With a suitable modifier the term *bronze* also extends to various copper-base alloy systems where the principal alloying element is other than tin or zinc. These systems include *aluminum bronzes*, *beryllium bronzes*, and *silicon bronzes*.

Nickel-silver, formerly known as German silver, is a copper-alloy containing both nickel and zinc. Its name derives from its predominantly silvery color. *Cupro-nickels* are essentially copper and nickel, the nickel content usually 10, 20, or 30 percent. In addition to these, there are many special and proprietary alloys that include *aluminum-tin bronze*, *aluminum-silicon bronze*, *cadmium bronze*, *chromium copper*, *beryllium copper*, *leaded copper*, and *selenium copper*.

Copper-base alloys are also grouped in two classes according to specifications required in the processes of fabrication. These two classes are wrought alloys and casting or foundry alloys. The *wrought alloys* of copper are regarded as only those made by alloying the various components and casting into slabs, cakes, or billets for hot or cold rolling, drawing, extrusion, or forging. *Casting alloys* are made from a complex assortment of industrial nonferrous scrap by scientific selection, smelting, and refining processes. Many compositions suitable for casting in sand or permanent molds are entirely unfit for working operations.

Designations of copper and copper-base scrap as given by the American Metal Market (*3*)[2] are—

No. 1 Copper Wire: Consists of clean, untinned, uncoated, unalloyed copper wire and cable, heavy field wire, heavy armature wire, not smaller than No. 16 B. & S. wire gage to be free from burnt copper wire which is brittle and foreign attachments.

No. 2 Copper Wire: Consists of miscellaneous clean copper wire which may contain a percentage of tin-coated, lead-coated, solder-coated wire, enameled wire, and copper wire with soldered ends. To be free of hair wire or burnt wire which is brittle. The tin-coated, lead-coated, solder-coated and enamel wire not to be over 15 percent of the total weight.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

MIXED HEAVY COPPER: Consists of copper clippings, clean copper pipe and tubing, copper plates and pieces, copper wire and segments, which may contain tin-coated, solder-coated, lead-coated copper scrap and copper scrap with soldered ends, but to be free of hair wire or burnt which is brittle.

LIGHT COPPER: Consists of the bottoms of copper kettles and boilers, bath tub linings, hair wire, burnt copper wire which is brittle, roofing copper and similar copper, free from radiators and fire extinguishers, brass and bronze screening, excessive lead and solder, readily removable iron, old electrotype shells, unclean gaskets and free of excessive paint, tar and scale.

COMPOSITION OR RED BRASS: Consists of red brass scrap, valves, machinery bearings and other parts of machinery, including miscellaneous castings made of copper, tin, zinc and/or lead, no piece to measure more than 12 inches over any one part or to weigh over 100 pounds, to be free of railroad boxes, and other similarly excessively leaded material, cocks and faucets, gates, hot pieces, ingots and burned brass, aluminum bronze, manganese-bronze and iron.

COMPOSITION TURNINGS: Consists of turnings from red brass composition material and should be sold subject to sample or analysis.

COCKS AND FAUCETS: Consists of mixed clean red and yellow brass, including chrome or nickel plated, free of gas cocks and beer faucets, and to contain a minimum of 35 percent red.

NEW BRASS CLIPPINGS: Consists of the cuttings of new unleaded yellow brass sheet, to be clean and free from foreign substances and not to contain more than 10 percent of clean brass punchings under ¼". To be free of Muntz metal and naval brass.

NO. 1 ROD TURNINGS: Consists of strickly rod turnings, free of aluminum, manganese, composition, Tobin and Muntz metal turnings; not to contain over 3 percent free iron, oil or other moisture; to be free of grindings and babbitts; to contain not more than 0.30 percent tin and not more than 0.15 percent alloyed iron.

BRASS ROD ENDS: Consists of new, clean rod ends from free turning brass rods and forging rods, not to contain more than 0.30 percent tin and not more than 0.15 percent alloyed iron. To be free of Muntz metal and naval brass or any other alloys. To be in pieces not larger than 12" and free of foreign matter.

AUTO RADIATORS: Consists of mixed automobile radiators, to be free of aluminum radiators, and iron finned radiators. All radiators to be subject to deduction of actual iron.

REFINERY BRASS scrap contains minimum of 60 percent copper, not more than 5 percent iron, with the balance made up predominantly of zinc; free of grindings.

TECHNOLOGY

Geology

Copper ore is found in many types of deposits that occur in a variety of host rocks. The period of their formation varies from Precambrian to Tertiary. Most of them are associated in time and place with igneous activity but the origin of some that occur in sedimentary rocks, seemingly far distant from such activity is the subject of some debate. Extrusive and intrusive rocks associated with many of the deposits are of intermediate composition and the intrusives—monzonite and diorite— have quartzoze and porphyritic phases.

Porphyry copper deposits account for a large percentage of the U.S. production and much of the world output. They contain most of the estimated commercial copper reserve of the world. Porphyry is used commonly to designate any igneous rock having larger crystals imbedded in a finer grained groundmass. It is more loosely and incorrectly applied in the mining industry to any igneous rock especially when occurring with ore. In a commercial sense the term "porphyry copper deposits" is not restricted to ore in porphyry but refers to deposits characterized by large size and uniform dissemination of copper bearing minerals through parts of the intrusive mass itself or through the adjacent rocks into which the porphyry has intruded. The ore minerals occur as isolated specks or in small veinlets. Porphyry deposits usually are low in average copper content and may contain gold, silver, molybdenum, and some minor metals in quantities sufficient to warrant their recovery. Many of the deposits were formed by secondary enrichment of lean primary ore by weathering or some other surficial processes, resulting from the downward percolation of copper-bearing solutions from which the copper was deposited at lower levels. Three zones resulted from this action, an upper or leached zone containing oxide minerals and underlain by a zone of enrichment which in turn is underlain by a zone of primary mineralization. Oxide and carbonate minerals occur in the leached zone; chalcocite as the principal mineral and lesser amounts of covellite are found in the zone of secondary enrichment; chalcopyrite and pyrite are the principal minerals in the zone of primary mineralization, which in some deposits contains sufficient copper to be ore. Some of the deposits do not have a great vertical range but the mine at Bingham Canyon, Utah, has attained a depth of more than 2,000 feet below the highest point of stripping. The major porphyry deposits of the world are in the Southwestern and Western United States, Chile, Peru, and U.S.S.R.; there are smaller deposits in Canada, Mexico and southeastern Europe. The first porphyry-type deposits to be developed in Africa is being prepared for production in the Republic of South Africa.

Associated with the porphyry deposits in time and frequently in place are vein, pipes, and bedded deposits in sedimentary rocks. Vein deposits were formed by ore minerals filling open fissures or replacing adjacent wall rock which had been brecciated by faulting or fracturing. The simplest veins are those which occupy a single fissure. Large deposits of this type are uncommon but the Magma and Old Dominion veins at Superior and Globe, Ariz.,

approach it. Vein systems are complex and intricate in other districts, such as Butte, Mont., and Morenci, Ariz. At least three ore-bearing and several non-ore-bearing fissure systems have been recognized in Butte. Some of the veins are large enough to be mined as a single unit; in some parts of the areas, however, several small veins are mined as a mass.

Bedded deposits in sedimentary rock include what are known as contact or pyrometasematic deposits and those formed by replacement of sedimentary rocks, frequently limestone, outward from fissures. The two types are not sharply separated. The typical contact deposit are replacements in limestone or dolomite by silicates, iron oxides, and sulfides of iron and copper. They occur at or near the contact of a sedimentary rock and an intrusive body. Replacement deposits are those in which certain beds of limestone are replaced outward from fissure with or without the formation of silicates. Part of the large deposits of Bisbee, Ariz. and the replacement deposits at Bingham Canyon, Utah, are examples of these occurrences and other deposits of less importance have been mined.

The copper ores of the central African copper belt, that contribute about 18 percent of the supply of copper, occur in sedimentary deposits underlain by metamorphic and igneous rock and overlain by younger sediments. The sedimentary beds have been faulted and folded into a series of complex anticlines and synclines. The anticlines have been eroded and the synclines form basins where concentrations of copper minerals are found. The deposits contain oxidized ore near the surface which grades through mixed oxide and sulfide ores to large deposits of sulfides at depth. The sedimentary deposits of Dzhezkagan in the U.S.S.R. are reported to be similar to those of Northern Rhodesia except they contain a little lead. The deposits occur in continental sandstones, shales, and conglomerates in which there are several ore-bearing horizons.

The deposits of the Precambrian Canadian shield are of the next importance economically. The nickel-copper deposits of Sudbury are perhaps the most unusual. The dominant geologic feature of the district is a spoon-shaped sheet of intrusive norite, which is underlain by an ancient complex of granite, gneiss, schist, metamorphosed sediments, and various eruptives. The nickel-copper ore occurs predominantly near the base of the norite but partly in underlying rocks as pyrrhotite, pentlandite, and chalcopyrite associated with pyrite and magnetite. Gold and silver occur in the native state and tellurides and platinum-group metals occur as arsenides and other rare combinations.

The native copper deposits of the Lake Superior area occur in shoots in the tops of certain lava flows, in conglomerates interbedded with the flows and in sandstone. Deposits of this type have substantial vertical depth with no notable change in mineralization. The ores are usually low-grade concentrating ores, although masses of copper are encountered. Other economic deposits in the area occur as disseminated chalcocite in beds of shale.

Lenticular deposits in schistose rock include those in which the primary mineralization consists mainly of sulfides of iron, copper, and zinc, commonly as replacement of the host rock. Such deposits usually are found where erosion has been deep and do not seem to be associated with igneous stocks. They occur in the Appalachian region, the western part of the United States, and British Columbia. Supergene alternation of such deposits usually produces a thin zone of enriched sulfides, as at Ducktown, Tenn. and Iron Mountain, Calif., but sometimes the enrichment is deep as at Jerome, Ariz.

Mineralogy

Copper is found in nature in numerous minerals and in various combinations with other elements. Of about 165 known copper minerals, only about 12 are commercially important; and 6 minerals are the source of over 95 percent of the copper mined. The principal copper minerals are as follows:

Mineral	Composition	Specific gravity	Copper, percent
Native: Native copper	Cu	8.8–8.9	100
Oxides:			
Cuprite	Cu_2O	6.0	88.8
Tenorite	CuO	5.8–6.3	79.8
Malachite	$CuCO_3Cu(OH)_2$	3.9–4.03	57.3
Azurite	$2CuCO_3Cu(OH)_2$	3.77	55.1
Chrysocolla	$CuSiO_32H_2O$	2.0–2.4	36.0
Antlerite	$Cu_3SO_4(OH)_4$	3.39	54.0
Brochantite	$Cu_4SO_4(OH)_6$	3.9	56.2
Atacamite	$CuCl_2·3Cu(OH)_2$	3.75–3.77	59.4
Sulfides:			
Chalcopyrite	$CuFeS_2$	4.2–4.3	34.5
Bornite	Cu_5FeS_4	4.9–5.4	63.3
Chalcocite	Cu_2S	5.5–5.8	79.8
Covellite	CuS	4.9–5.0	66.4
Enargite	Cu_3AsS_4	4.43–4.45	48.3
Tetrahedrite	$Cu_8Sb_2S_7$	4.7–5.0	52.1
Tennantite	$Cu_8As_2S_7$	4.7–5.0	57.0

Copper-bearing minerals are classified in three important groups. Primary or hypogene minerals are those deposited at depth in the earth by processes that may be related to igneous activity. Examples of these are bornite, chalcopyrite, and enargite. Some complex minerals are also primary, but minerals of this type are not abundant in economic deposits. The second group is composed of oxide copper supergene minerals commonly formed by weathering of copper sulfides exposed to erosion. Cuprite,

malachite, azurite, and chrysocolla are the chief minerals of the supergene zones of copper deposits where a reactive gangue is present. Brochantite and atacamite are found in the upper portions of ore bodies in arid regions. The third group, the simple sulfides, chalcocite, and covellite, are predominant in the zone of secondary enrichment. These minerals are formed when copper is leached from sulfides near the earth's surface, carried downward in solution, and precipitated at water level.

The copper minerals found most frequently at the surface are the green and blue copper carbonate and the green silicates. These colors are distinctive and rock with a very small percentage of copper may be vividly green. Cuprite, tenorite, native copper, atacamite, chalcanthite, and occasionally other rare copper minerals are found in outcrops; these minerals, together with the carbonates and silicate minerals, are formed by the weathering of copper sulfides. Chalcopyrite and, to a smaller extent, bornite may exist in outcrops or in float, but when found at the surface in arid districts usually they are in the form of kernels surrounded by alteration products. Copper sulfides usually are associated with pyrite and other iron sulfide minerals.

Copper ores vary in type (whether sulfide or oxide), in the valuable metals occurring in them, in their tenor, and in the kind of associated gangue present. They are commonly distinguished as oxidized ores or sulfide ores. These may range between high grade and low grade, which roughly expresses their copper content.

A large percentage of copper produced comes from sulfide ore deposits which are natural mixtures containing copper-bearing sulfide minerals and associated gangue minerals that are either of valueless mineral content or of subordinate economic importance. These ores comprise three groups. In the first, ore minerals of the porphyry and central African types are chalcocite, chalcopyrite, and bornite associated with pyrite. The second group consists of the cupriferous pyrite bodies which contain abundant pyrite and pyrrhotite. Notable examples are at Jerome, Ariz., Rio Tinto, Spain, and the island of Cyprus. The ores of the third group carry some of the copper in enargite or tenantite which contains arsenic. Well-known deposits of this type are at Butte, Mont., Bor, Yugoslavia, and Tsumeb, South-West Africa. The gangue may consist simply of the minerals making up the host rock, or it may be composed of various other minerals developed during the the general ore-forming process, or it may occur as a combination of these two groups. Thus the gangue might consist of a sulfide, such as pyrite, along with quartz, sericite, calcite, barite, etc. From an ore like this, in addition to the principal value in copper, pyrite might be reclaimed as a byproduct for its sulfur, and barite might be recovered to be used in well-drilling muds.

An oxidized copper ore is also a natural mixture of oxidized copper minerals and gangue. Examples would be the deposits of malachite and azurite ores in dolomite of the Congo (Léopoldville) and the unusual oxide mineral assemblage at Chuquicamata, Chile, consisting of atacamite, brochantite, and other sulfates.

Native copper frequently occurs in small quantities in the zone of oxidation, but in a few deposits it is the ore mineral. In these deposits the gangue may be conglomerate or basalt, as in the ores from the Lake Superior district in Michigan, or sandstone, as in the much smaller deposits at Corocoro, Bolivia.

Prospecting and Exploration

Prospecting is the search for ore occurrence, and exploration is the work involved in gaining knowledge of the size, shape, position, and value of an ore body. These two activities, although quite different in purpose, use the same tools. From a practical standpoint, separation of prospecting from exploration is difficult and consequently prospecting and exploration of copper deposits are treated herein as a unit. Most copper mines have been discovered by surface prospecting often using distinctive coloration of rocks as a guide. However, the exploration responsible for the development and expansion of many of the mines resulted from costly geologic and geophysical investigations, exploratory drilling, and excavation of underground workings.

Tracing float, trenching, and test pitting were the usual methods formerly used. Large exploration companies now use geochemistry, airborne geophysical methods, and photogeology to select areas for preliminary exploration. Favorable appearing areas are studied more intensively by checking geophysical anomalies using corresponding ground techniques, detailed geochemical work and geological mapping, and possibly shallow drilling, pitting, stripping, and trenching. If results are encouraging, more intensive exploration is conducted, usually to obtain representative samples. The exploratory program is expanded to delineate the ore body, determine its grade and mineralogic nature, plan mining methods and equipment installation, project the scale of operation, and investigate other technical and economic factors essential to the establishment of a mining enterprise.

Geophysical prospecting is used to measure and interpret anomalous physical or physio-

chemical phenomena within the earth's crust. It utilizes electric, gravimetric, magnetic, seismic, and thermic properties of rocks and minerals, either those natural to them or produced artificially. Geophysical methods disclosed information that encouraged the development of three outstanding ore bodies; Pima mine in Arizona where an ore body lays beneath 200 feet of valley fill; the buried Lynn Lake nickel-copper deposit; and the copper-zinc-silver deposits discovered in 1963 north of Timmins, Ontario.

Exploration to define the size and configuration of a newly found ore body and to determine its mineral content is usually accomplished by boring. The principal types of drills used for this purpose are churn drills, rotary drills, diamond drills, and percussion drills. Diamond drilling is most widely used because of its speed, adaptability for directional drilling, and recovery of core for analysis and other studies. Approximately one-half of the exploratory and development work done in 1963 on domestic copper deposits was accomplished by core drilling and about one-third by rotary drilling.

Mining

Open-pit (or open-cut) and underground methods are used in mining various types of copper deposits. Open-pit mining accounted for 74 percent of the copper and 81 percent of the ore mined in the United States in 1963. The choice of method is determined by the size, configuration, and depth of the ore body, which largely determine the relative costs of mining by the two methods. Topography, climate, existing surface improvements, availability of skilled labor, and availability of capital also affect the choice of method. Large porphyry-type deposits are amenable to surface mining if they are near enough to the surface so that the cost of removing overburden is not prohibitive. If the ratio of waste-to-ore is too large, these deposits are mined by caving methods by which low costs are achieved through mass production. Veins and deposits of lenticular or tabular shape usually are mined by underground workings that permit extraction of a large percentage of ore and provide support of the workings to prevent loss of ore in adjacent ore bodies or the destruction of surface installations.

Although open-pit mining appears simple, good management and careful planning are essential to achieve low mining costs. The shape and position of the ore body must be predetermined to allow planning for access, stripping disposal, bench design, pit slopes, transportation, equipment, and other requirements of handling large quantities of ore and waste. The advantages of open-pit mining are the ease with which the rate of mining can be changed, low shutdown expense, the ability to mine selectively, practically complete extraction of ore within pit limits, a high rate of productivity by labor, and elimination of many hazards inherent to underground mining. Disadvantages of the method are heavy capital outlay for equipment and, where the amount of overburden is large, a corresponding capital expenditure for stripping. Time lapse between the beginning of stripping and actual production may be quite long and can be a disadvantage if market conditions change adversely during the development period.

Benches in open-pit copper mines range from 25 to 60 feet. The height is selected to give maximum digging efficiencies, but may be controlled by ore-waste separation. Hardness of rock and stability of faces also affect the height.

The cycle in open-pit ore extraction consists of drilling, blasting, loading, and transportation. Primary drilling is sinking vertical or near vertical blast holes behind the face of an unbroken bank. Secondary drilling is required to break boulders too large for shovels to handle or to blast unbroken points of rock that project above the digging grade in the shovel pit. Recent advances in drilling and blasting include the use of rotary drills instead of churn drills and use of lower cost ammonium nitrate, sensitized by diesel fuel or some other suitable petroleum product as an efficient blasting agent.

Ore and waste are loaded by full-revolving power shovels. At many mines, shovels with 4- to 6-cubic-yard capacities are used but large mines have shown a tendency to use 7- to 10-yard shovels, and two 12-cubic-yard shovels were installed recently at the Utah Copper mine.

Haulage is by truck of large capacity for short hauls and by train for longer ones. However, the trend is toward more of the haulage by larger trucks. Overburden and ore are moved at some mines by tractor-drawn scrapers which have been useful in preparing approaches or drop cuts. Skip-ways and belt conveyors have been installed at other mines for ore handling.

A substantial portion of the world production is mined from deep deposits by underground methods which are designed for the extraction of ore with the greatest safety at minimum costs. Most of the modern underground mining of copper is done by two methods, caving and supported stopes.

Caving methods are of three distinct types, block caving, top slicing, and sublevel caving. Block caving is a low-cost mining method amenable to mass production from large, homogene-

ous, and rather weak ore bodies. The use of the method requires detailed engineering study of an ore body by systematic and extensive exploration and sampling. Adequate development, preparatory work, transportation systems, and ore drawing control are equally important. This method consists of dividing suitable ore bodies into blocks of predetermined size and undercutting each to permit rock stresses to cave and crush the ore to sizes that can be handled easily. The method is nonselective and lean sections of ore and waste will be broken and drawn with the ore. The method also results in some loss of ore. Top slicing is an important modification of caving where ore is extracted by excavating a series of horizontal or inclined timbered slices, beginning at the top of the ore body and progressing downward. After each slice is mined out the overlying rock is caved by blasting the timber supports or allowing them to crush. The floor of each slice is covered with a mat of timbers to separate the caved material from the solid ore beneath. Top slicing is more costly than block-caving but allows recovery of almost all the ore and is applicable to smaller and more irregular ore bodies. Sublevel caving is somewhat similar to top slicing in that ore is mined progressively downward in horizontal slices. The fundamental difference is that the slices are thicker in sublevel caving. The method is rarely used in copper mining.

Supported stopes are of two types, naturally supported and artificially supported. The simplest form of naturally supported stopes are open stopes in which the entire ore body is removed from wall to wall without any support other than occasional props, stulls, or cribs to hold local patches of insecure ground. The method is applicable to relatively small ore bodies with strong walls and roofs. Open stopes with pillar support are used when extracting ore from wider ore bodies or those that occur as bedded deposits. Pillars of definite size and spacing are left in room and pillar methods of mining. Sometimes low-grade portions of the ore are left as pillars.

Artificially supported stopes are those in which installation of systematic temporary or permanent support of ground is part of the mining cycle. Three principal types are used in copper mining.

Shrinkage stoping is applied to relatively thin, tabular deposits dipping at angles greater than 50°, having few waste inclusions and firm walls that stand well without sloughing. Ore is mined in successive horizontal or inclined slices, working upward from the bottom of a block of ore. Only enough of the broken ore is drawn from the stope after each cut or slice to allow working space between the broken and unbroken ore. The broken ore serves as a floor upon which to work when drilling for the next successive cut and also provides supports for the stope walls. After mining has been completed to the upper limits of the block, all ore is drawn leaving the stope empty.

Cut and fill stoping is applicable for extracting firm ore from deposits enclosed in walls, one or both of which may be weak. It is used also to mine deposits too irregular to be mined by shrinkage stoping. Ore is excavated by successive flat or inclined cuts working upward as in shrinkage stoping, but the ore is removed after mining each slice. The slice is then partly filled with waste rock, milltailing, sand, or other material to support the walls, leaving a working place for mining the next slice.

Timbered stoping is used to mine regular or irregular ore bodies in which the ore and/or the walls are too weak to stand for a brief time over a short span and where caving of adjacent rock must be prevented. The most elaborate method of timbered stoping is the square-set method by which the back and walls are supported by framed timber forming a network of contiguous, hollow rectangular prisms, in the place previously occupied by ore. The ore is removed in small, rectangular blocks, usually just large enough to provide space for a set of timber. Usually stopes are mined in floors one above the other and the timbers of one floor are framed into those of the lower one. Timbered stoping is usually accompanied by filling and, in heavy ground, the sets are filled with waste promptly after they are installed.

Beneficiation

Some copper ores of sufficient copper content are smelted directly. However, nearly all the copper now produced, or that will be produced in the near future is from sulfide, oxide, or native copper ores that are first subjected to a physical separation of minerals by upgrading processes known as milling or concentration. The principal steps in concentration are crushing, grinding, and separation of valuable minerals from waste material. The products of upgrading are: a concentrate, which contains most of the ore minerals and some gangue; and tailing which contains the waste material and a portion of valuable minerals. The method of separating copper minerals from gangue is determined by the chemical form, size, density, and surface characteristics.

At concentrators of large capacity, sulfide minerals are recovered by flotation, a highly developed and universally used process. Some small operations, however, employ gravity

methods such as jigs or vibrating tables. Flotation involves the separation of different mineral particles from each other in a liquid pulp. Finely ground ore is agitated in water with air or other gases. Various oils and chemicals are added to cause the selected minerals to adhere and rise to the surface where they are removed in the froth. Other minerals remain suspended in the pulp. Originally, recovery of valuable minerals in only one product was accomplished. With the advancement of the art, the principle of selective flotation was evolved and two or more relatively clean products can be recovered from complex material. Typical selective or differential flotation practices in copper milling are separation of copper sulfides from pyrite, recovery of molybdenum from copper concentrate, and recovery of a copper concentrate from complex lead-zinc-copper ore. More than 90 percent of the copper contained in the ore is recovered at large concentrators using good milling practices. To a certain extent, the copper content of the concentrate is related to the mineralogical composition of the ore treated, thus ore with chalcocite as the principal mineral should yield a higher grade concentrate than one containing chalcopyrite and pyrite. The copper content of concentrates produced in the United States ranges from 20 to 35 percent.

The treatment of mixed ore, containing both sulfide and oxide minerals, depends on the relative proportions of the two types of minerals. If sulfides predominate, flotation is used, employing reagents that favor flotation of oxide minerals. When the ore contains almost equal amounts of sulfide and oxide minerals, combinations of leaching and flotation are used. By one method, the ore is leached with sulfuric acid and the residue is treated in a concentrator where sulfide minerals are recovered by flotation. In another process, leach-precipitation-float (LPF), the oxide minerals are converted to metallic copper which readily responds to flotation with sulfide minerals. Sponge iron is usually used to precipitate copper prior to flotation.

Recovery of copper carbonate minerals either alone or with copper sulfides by sulfidation and flotation has been achieved with a certain degree of success. Leaching, however, is the method usually used in the United States to recover copper from oxide minerals.

Leaching oxide or mixed oxide-sulfide ores is unfeasible if the gangue is acid consuming and the economic flotation of silicate minerals remains unsolved. Research by the Bureau of Mines on the segregation process and by an African company on TORCO (treatment of refractory copper ores) shows promising results. The two processes are similar in that they involve heating ore with a halide salt and carbonaceous material. Basically the process proceeds in four stages: decomposition of salt and formation of hydrochloric acid; the acid and copper minerals form volatile cuprous chloride; the cuprous chloride is reduced to metallic copper on the carbon particles; and the metallic copper is recovered by flotation.

Recent improvements in milling practices include automation, autogenous grinding, and classification by cyclones.

Leaching

Copper produced in the United States from oxide ores is recovered principally by hydrometallurgical methods. Excluding copper produced from oxide minerals by the LPF process, production by leaching is approximately 9 percent of the U.S. output. The usual practice is to leach oxide ores with dilute sulfuric acid, but leaching mixed oxide-sulfide ore is more difficult. Ferric sulfate is an active solvent of most oxidized copper minerals and to an extent is effective on free copper sulfides. Certain bacteria have important and beneficial action during leaching.

Four principal methods of leaching are used in the treatment of copper ore: (1) leaching in place; (2) heap leaching; (3) leaching by percolation; and (4) leaching by agitation. The choice of method is dependent upon disposition and grade of ore to be treated as well as the character of the associated gangue. Ore bodies that contain sulfide minerals and are shattered and broken so that air and water have access to the ore are suitable for leaching in place. The copper sulfide minerals exposed are subjected to natural oxidation by alternate and intermittent contact with air and water to form water-soluble copper sulfate. The leach solution is accumulated in drainage tunnels driven under the ore body or in the lower workings of the mine. Leaching in place has been successfully applied in mines at Butte, Mont.; the Miami and Ray mines in Ariz.; the Eureka mine, Ducktown, Tenn.; the Cronebane mine, Wicklow County, Ireland; and the Aznalcollar and Rio Tinto mines in Spain. The operations of the Ohio Copper Co. at Bingham Canyon, Utah, in the early 1920's is a classical example of leaching in place at a domestic copper mine. Heap leaching is similar to leaching in place in that it depends on the natural oxidation of the sulfide minerals by continual contact with air and water. Oxide, sulfide, and mixed ores, containing some copper values but which are too low grade to be processed profitably by any other method and which must be removed to permit mining, are treated by heap leaching. The

process consists essentially of piling or dumping leaching ore, without crushing or other preparation, on an area having proper drainage to natural or prepared basins. Leach solutions are directed over the piles and allowed to drain through the heap. The sulfide minerals that have been oxidized to sulfates are dissolved in the leaching solution which collects in the prepared basins. Copper is recovered from the pregnant leach solution by cementation on scrap iron. After removal of the copper, the spent solution is returned to the piles for another cycle of leaching. Percolation leaching is another important hydrometallurgical method for recovery of copper from large deposits of low-grade ore. Ore charged to a number of leaching vats is successively treated with leaching solution, either by upward or downward percolation, or both. Usually the leach solution enters a vat at the bottom, percolates upward until the ore is flooded, is held there for a soaking period, and then drained and advanced to the next vat where the process is repeated. The flow of the leach solution in this sequence completes a single cycle. The number of cycles necessary for optimum extraction depends upon the solubility of the copper minerals in the ore. Agitation leaching is applicable to those ores that cannot be effectively treated by percolation or to those operations where efficient extraction is required at a rapid rate. Dissolution of the copper minerals is effected by keeping finely divided ore particles in suspension in the solvent. Agitation is accomplished either mechanically or by forced air and must be strong enough to prevent settling in the tanks.

Copper is recovered from leach solution by electrolysis or by precipitation with iron. The iron is usually in the form of shredded and detinned cans, detinned plate, or sponge iron. This form of precipitation is termed cementation and the copper precipitate is called cement copper.

Some copper is obtained by ammoniacal leaching of native copper ore or tailing in Michigan. In the process, the coarser native copper is recovered by gravity concentration followed by classification and separation into plus and minus 100 mesh material. Fine native copper is removed from the minus 100 mesh pulp by flotation. The plus 100 mesh sand is treated by batch, downward percolation leaching method in which cupric ammonium carbonate is the active leaching agent. An excess of ammonia is required to prevent the complex salt from hydrolyzing. The copper is recovered by simple heating to drive off the excess ammonia and the complex salt decomposes in the solution with the precipitation of copper oxide.

Smelting and Refining

Because most of the world copper production is extracted from low-grade sulfide ores that require concentration, the dominant smelting processes for recovering copper metal are adapted to treating fine-grained sulfide concentrate. The usual concentrate consists mainly of copper and iron sulfide minerals, and gangue, and the purpose of smelting is to separate copper from the iron, sulfur, and gangue. Copper's strong affinity for sulfur and its weak affinity for oxygen as compared with iron, sulfur, and other base metals in the ore form the basis for the three major steps in smelting—roasting, reverberatory furnacing, and converting.

The object of roasting sulfide ores or concentrates of copper is to oxidize sulfur and iron and to remove volatile impurities such as antimony, arsenic, and bismuth. Copper and iron sulfides are among the easiest of the common metallic sulfides to convert to oxides. Mixtures of copper and iron sulfides relatively free from inert compounds are readily ignited and will roast autogenously to 6 to 8 percent sulfur without further application of heat. However, by modern practice, the concentrate produced from some sulfide ores is controlled at the concentrator to avoid the need of roasting before reverberatory smelting. Roasters were not installed in some of the newer smelters and roasters at some of the older ones are used now as dryers. It is apparent that roasters are gradually being abandoned in copper smelting.

Roasted or unroasted materials are heated in reverberatory furnaces, which are long, room-like structures. The fuel and the charge, consisting of copper-bearing material and flux, are kept separate. Oil, gas, or pulverized coal is burned in a separate compartment from which the flame and hot gases pass over the charge. Heating of the charge is accomplished by radiation from the roof and walls rather than by direct contact with the hot gases. In this reducing or neutral atmosphere, copper and iron form the stable copper sulfide Cu_2S. Excess sulfur unites with iron to form a correspondingly stable ferrous sulfide. The two sulfides are miscible in all proportions in the liquid state and form a eutectic in the solid state. The mixture, either liquid or solid is known as copper matte. Excess iron in the form of ferrous oxide, combines with silica and enters the slag.

A few plants still use blast furnaces in smelting copper ore because they are useful under certain conditions. The feed to blast furnaces are ores more than an inch in size or fines that have been sintered. The furnace is essentially a long, narrow upright shaft. The molten

products, matte and slag, collect and are drawn off the bottom, and new material is charged at the top to keep the charge-level relatively constant. Coke is usually the fuel and is mixed with the ore and flux. A crucible is used as a collecting trough through which matte and slag flow to a forehearth or settler in which the slag rises and is removed almost continually.

Electric smelting of copper is used to produce matte where the cost of electric power is less than coal or other fuels. The chemistry of electric smelting is essentially the same as in reverberatory smelting.

Converting is the final stage in the process of smelting copper sulfide ores or concentrates and is accomplished by blowing thin streams of air through the molten matte (the product of the reverberatory or blast furnace) in a refractory-lined converter. Converting is a batch process and requires two stages.

The first or white-metal stage of converting is rapid oxidation of the iron sulfide in the matte to iron oxide and sulfur dioxide. Enough silica is supplied to form an iron silicate slag. The copper remains as copper sulfide until most of the iron has been oxidized. When slagging is complete, the slag is poured off, leaving molten copper sulfide—known as white metal at this stage. Blowing is then continued to oxidize the sulfur in the white metal leaving metallic copper. Converter slag contains 2 to 5 percent copper and is returned to the smelting furnaces for retreatment where its high iron content is generally an aid to fluxing. When the converter cycle is finished the converter is tilted to discharge the copper metal into ladles in which it is transferred to the anode furnace and casting machines. Due to the rough upper surface when solidified, the product of the converter is known as blister copper. The blister copper contains most of the precious metals and minor quantities of other elements in the charge; hence, it is refined before marketing.

Special methods of treatment are required for smelting native copper ores. Formerly, the concentrate was smelted in blast furnaces, but present output is treated almost entirely in reverberatory furnaces. The charge, consisting of concentrate, metal, coal for reducing, and if necessary limestone for flux, is fed through two holes in the top of the furnace. It takes about 24 hours to melt the charge and form slag, after which the metal is tapped into a refining furnace which is placed at a lower level.

Copper produced by smelting is too impure for most applications and requires refining before use. This crude copper is classified as blister copper produced from matte, or black copper produced from the smelting of oxidized ores or native copper ores. It contains silver and gold, and other impurities such as arsenic, antimony, bismuth, lead, selenium, tellurium, and iron. The amount of these impurities varies greatly depending upon the character of the ore and the degree of elimination in smelting and converting.

Two methods are used for refining copper, one by fire and the other by electrolysis. In general, electrolytic refining, which is more expensive, will be used when the amount of precious metals or the amount and character of the impurities present warrants. Most of the world production of primary copper, however, is processed by electrolytic refining followed by the melting of cathodes in fuel-fired reverberatory furnaces.

The fire-refining process employs oxidation, fluxing, and reduction. It is based on the weak affinity of copper for oxygen as compared with that of the impurities. Compressed air at 8 to 10 pounds pressure is introduced under the molten metal surface through iron pipes, causing a bubbling and agitating action. This exposes the molten copper to the furnace atmosphere and cuprous oxide is formed. The copper oxide dissolves in the metal bath, reacts with the copper sulfide present forming sulfur dioxide which escapes from the melt; the copper oxide also gives up its oxygen to certain impurities, forming metallic oxides which combine with added silica to form slag. Sulfur, zinc, tin, and iron are almost entirely eliminated and many other impurities are partially eliminated by oxidation. Lead, arsenic, and antimony can only be removed in large quantities by fluxing. The remaining copper oxide is reduced by partially covering the molten metal with coke and inserting green wood poles through the furnace door forcing one end below the bath surface. As fast as a pole burns away it is fed into the furnace until consumed. Reducing gases formed by combustion convert the copper oxide in the bath to copper. The progress of reduction from about 0.90 percent oxygen to the required tough-pitch content (0.02 to 0.05 percent) is determined by appearance and microscopic examination of samples. A new method of reduction using reformed natural gas has been developed by the Phelps Dodge Corp. Czechoslovakian engineers recently obtained a patent for the use of ammonia as a reducing agent in fire refining of copper.

The common sequence of electrolytic refining operations is fire refining of converter copper to produce purer and more homogeneous anodes, electrolytic refining of the anodes to recover precious metals and remove impurities, and a second fire refining to adjust the physical properties of the electrolytic copper to be cast in shapes for use in industry. In the electrolytic

refining process copper is separated from other metals and impurities by electrolytic oxidation and deposited as pure metal by electrolytic reduction in an electrolyte which is essentially a solution of copper sulfate and sulfuric acid. Anodes and cathodes are hung alternately, at carefully spaced intervals, in concrete electrolytic cells containing the electrolyte. When current is applied copper is dissolved from the anode and enters the electrolyte as $CuSO_4$ (electrolytic oxidation); at the same time an equivalent amount of copper plates out of solution on the cathode (electrolytic reduction). Many of the usual impurities—such as gold, silver, platinum group metals, and the selenides and tellurides of metals—fall to the bottom of the tank and form anode slime or mud; other impurities—arsenic, antimony, bismuth, and nickel—enter the electrolyte and necessitate close control of temperature and the copper and acid content of the electrolyte.

USES

A variety of properties are responsible for copper's important role and diversity of use in the industrial economy. Properties of copper having major significance are its high electrical and thermal conductivities, corrosion resistance, good ductility and malleability, and high strength. In addition, copper has a pleasing color, is nonmagnetic, and is easily finished by plating or lacquering; it can be welded, brazed, and soldered satisfactorily. Certain of these basic properties can be improved for many applications by alloying with other metals. As a consequence the popular commercial brasses, bronzes, copper-nickel alloys, and nickel silvers have been developed.

The use of copper and its alloys is universal. They are practically synonymous with all things electrical and have a myriad of uses in construction, autos, aircraft, missiles, railroad equipment, marine equipment, appliances, machinery and equipment, scientific instruments, utensils, jewelry, cladding, and many other applications.

Approximately half of all copper consumed is for electrical applications, including power transmission, electronics, electrical equipment, transportation, and complex weapons systems. Construction (homes, plants, office buildings) and power generation and transmission are the largest users. Virtually all building wiring is copper, as are most droplines leading from main power cables. The transmission of power continues to be a major market for copper. Although aluminum is now used for most high-voltage overhead lines, copper still dominates in high-voltage underground lines. Generation and utilization of electrical energy requires extremely large quantities of copper. Examples are heat exchangers, windings in motors, generators and transformers, magnet wire in control apparatus, and bus bars.

For communications, telephone and telegraph wire and cable are two of the biggest markets. Its excellent electrical conductivity has made copper the major metal used in the expanding applications of printed circuits. Numerous components in radio and television sets and telegraph receiving and sending equipment are made of copper or its alloys; and coaxial cables employ a substantial amount of copper. There is a large potential for the use of printed circuits in automobile instrument panels, appliances, and computers.

The noncorrosive quality of copper and its alloys accounts for many uses in construction for roofing products, plumbing goods, builders' hardware, and functional decorative applications. Sheet roofing, gutters, downspouts and heads, flashing, fittings, and accessories consume a large amount of copper. Additional architectural uses for construction and decorative purposes include balustrades, columns, doors, and screens. Copper and red brass are found frequently in plumbing items such as tank lever lift arms, toilet tank trim, lavatory fittings, tub fittings, faucets, traps and drains, flush valves, piping and tubing, and other fixtures. Brass and bronze are popular for builders' hardware because they are decorative, noncorrosive, and easy to fabricate for such items as locks, door knobs, door knockers, door stops, hinges, bolts, latches, and hasps.

The automotive industry accounts for about 9 percent of the copper consumed in the United States, using about 30 to 40 pounds per vehicle. Volume uses are in radiators, heaters and defrosters, air-conditioning units, bearings, bushings, carburetors, oil lines, strainers, wiring, switches, and plating. Major uses take strip, tube, plates, and wire; secondary uses take rods, bars, and foundry products.

The maze of wiring in the electrical systems of airplanes takes more copper than any other use in the aircraft industry. Some of the larger planes use up to 3,000 pounds of copper in the electrical systems and mechanical components.

Copper is a minor, though essential, metal in missiles. As in aircraft, the major use is in wiring systems.

Railroads use a large quantity of copper in diesel locomotives, passenger cars, and switching and signal devices. The average pullman car uses almost 2,000 pounds of copper tube in the water supply system, air brakes, heating system, air-conditioning unit, condensers, evaporator, and heating coils.

Tankers, cargo ships, pleasure craft, passenger liners, and naval vessels use copper and its alloys in a great variety of marine equipment. Naval brass is used for propeller shafting (because of its strength, torque resistance, machinability, and corrosion resistance); manganese bronze for struts and rudders (high strength and corrosion resistance); silicon bronze for fastenings and water tanks; and soft- and hard-drawn copper for exhaust yokes, fuel lines, water lines, and piping (resistance to corrosion and leaks, workability, long life). The U.S. Navy's nuclear submarines use brass in capstans, torpedo tubes, diving gear, and valves; more than 48,000 feet of copper tube in hydraulic, air, and lubricating oil lines; and cupro-nickel tube in auxiliary cooling lines, heat exchangers, lavatories, bilge pumps, and salt water service lines.

In the appliance field, manufacturers of washing machines, air-conditioning units, refrigerators, radio and television sets, and other units specify copper and its alloys for many components requiring materials that are electrically or thermally conductive, corrosion resistant, and durable.

Large machinery and equipment, turbines, and heat exchangers use copper or its alloys in many ways. Specific uses are copper for motors, other electrical equipment, and tubing; bronze for worm wheels, oil baffles, check valves, and levers; cupro-nickel for tubing; naval brass, muntz metal, and aluminum bronze for plates, sheets, bars, and weld wire.

Copper is used extensively in watches, clocks, microscopes, projectors, and many types of gages.

Solid copper, brass, and bronze are popular materials in utensils, jewelry, furnishings, and decorative items. They are used in the manufacture of such items as brass and bronze medallions; solid brass furnishings, including towel bars, curtain rods, wall hooks, and soap-dishes; cookware; table ware; and bronze and brass plaques and signs.

TABLE 2.—*Copper use pattern in 1960*

	Percent of total
Electrical equipment	19
Light and power industry	18
Building construction	16
Industrial equipment and supplies	10
Motor vehicles	9
Communications	6
Military	6
Household appliances	3
Railroad and marine	3
Electronics	3
Scientific	2
Miscellaneous	5
Total	100

Source: Kennecott Copper Corp.

Products of the powder-metallurgy process have found wide usage in machine components. Compacted structural parts are used in automotive, railroad, farm, aircraft, marine, and communications equipment and in household appliances such as, washers, dryers, ironers, electric fans, and refrigerators. Metal powder of single elements, or in combination with other metals or nonmetals, are processed to make oil-impregnated porous bearings, cams, gears, motor brushes, clutch facings, contact points, filters, filaments, lock assemblies, and many other various shapes. The number of automotive applications for powder-metal parts has doubled since 1950. Iron powder mixed with copper, or copper and carbon, is used for transmission and engine parts that receive high impact and fatigue loads. Many new applications are believed feasible as powders and processing methods are designed for strength properties.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

About 98 percent of the U.S. mine production of copper is recovered from copper ore; and the remainder from complex ores. In addition to copper, important quantities of byproduct, gold, silver, sulfuric acid, molybdenum, selenium, tellurium, arsenic, and platinum-group metals are recovered. These byproducts or coproducts may be recovered at one or more of the various steps of concentration, smelting, and refining. About 27 percent of the 66 million pounds of molybdenum produced in 1963 was recovered as a byproduct largely from copper ores. About 866,000 pounds of the 928,000 pounds of selenium and 152,000 pounds of the 201,000 pounds of tellurium produced in 1963 were recovered from the electrolytic production of copper; and 358,000 tons of sulfuric acid was produced at copper plants (includes output of a lead smelter). In the 5-year period 1959–63 approximately 32 percent of the United States gold production and 28 percent of the silver production were derived from the processing of copper ores.

More than 42 percent of the copper output in Canada comes from ores of Manitoba and Ontario, mined principally for nickel, and approximately 65 percent of the world's cobalt production in 1963 came from processing Belgian Congo copper ores. It was reported that 46 percent of the molybdenum produced in the U.S.S.R. in 1959 came from copper-molybdenum ores. Some of the ores contain five times as much molybdenum as those in the

United States with the best molybdenum content.

ALTERNATE MATERIALS

Aluminum is the principal alternative material for copper as an electrical conductor. Price is one of several factors that influence its partial substitution for copper. Aluminum wire with a steel core (ACSR) has displaced copper for long-distance transmission lines. Other typical substitutions of aluminum for copper are in bus bars, fractional horsepower motor windings, and lightbulb bases. There has been an accelerated shift to the use of steel for brass in shell cases.

Aluminum and stainless steels have also somewhat reduced the use of copper in the building industry. Technology has furthered substitution for copper by the introduction of the numerous clad metals, including copper clad, which use proportionately less metal than would solid copper. Printed electrical circuits have also come into the field as a substitute for copper wire and plastic tubing replaces copper in some automobiles and appliances and other uses.

SECONDARY SOURCES AND RECOVERY

Secondary copper is recovered from copper scrap, copper-alloy scrap, and other copper-bearing scrap materials. The term includes refined copper or the copper content of copper-base alloys, copper-bearing alloys, chemicals, and compounds. Although some brass is smelted for the separate recovery of its copper content, a large percentage of reclaimed brass is remelted into brass ingots that are sold as brass in the secondary market. The copper content of the scrap substitutes for primary copper in industrial and commercial products and thus may be classed as secondary copper.

Secondary copper is recovered from two principal classes of scrap, old scrap and new scrap. However, only old scrap is available from the accumulating reserve of secondary copper through reclamation of copper, brass, bronze, and other alloy products that have been used and then discarded because they are obsolete, worn out, or damaged. Such articles are wire, fired cartridge cases, pipe, automobile radiators, bearings, valves, screening, and lithographers' plates. Old scrap is collected by several thousand dealers who for the most part are not affiliated with primary copper producers.

The new scrap generated in fabricating and manufacturing semifinished and finished products from primary copper and copper-base alloy forms does not form a reservoir supply to supplement the production of primary copper. Examples of new scrap are defective castings, clippings, punchings, turnings, borings, skimming, drosses, and slag. Such scrap represents a circulating quantity of copper previously accounted for as supply of primary copper and returned to the fabricating process without reaching the product stage. However, data on the movement of new scrap have significance as indicators of business activity in the fabricating and scrap reclamation industries.

Channels through which much of the reclaimed copper returns to industry from scrap dealers and fabricators are brass mills, brass and bronze ingot makers, secondary and primary smelters and refiners, and foundries.

Total secondary copper production in 1938 was slightly less than 500,000 tons. By 1943 production had more than doubled and the all-time peak of 1,100,000 tons was attained. From then through 1958 output was relatively uniform and averaged 905,000 tons a year. Production declined to 849,000 tons in 1961 and rose to 974,000 tons in 1963.

More than two-thirds of the secondary copper is recovered in alloys, principally in ingots of brass and bronze, with lesser quantities alloyed with aluminum, iron and steel, and other metals. Most of the remainder of the annual output is recovered as refined copper, copper powder, and castings. Approximately 1 percent of the secondary copper output is in chemical compounds.

Copper and copper-base alloy scrap is sorted and separated into its various classifications. The separation is made on the basis of color, hardness, magnetic properties, type of fabrication, reaction to acids and other reagents, and original source. Brass scrap is sorted piece by piece. Like materials are grouped, assayed, and stored according to composition and metallic content. Furnace charges are made up of weighted amounts of one or more types of scrap that will closely approximate the desired composition of the alloy to be cast. After the charge has been melted a sample of the bath is taken and refining, consisting of fluxing, oxidation and slagging is started. After refining calculated additions of virgin metals are made to adjust the analysis of the melt to specifications and the heat is tapped and poured into ingots.

A substantial quantity of clean copper scrap is remelted, cast into anodes, and electrolytically refined. Other copper scrap is charged to reverberatories at primary smelters and is recovered as electrolytic or fire refined copper.

The major uses of copper in the principal foreign consuming countries are about the same as

those in the United States with a similar relationship between consumption of scrap and total copper. Further, scrap is collected, marketed, and processed in foreign countries in much the same manner as it is in the United States. This is particularly true in Europe where 40 to 45 percent of the world copper is consumed, principally in Great Britain, West Germany, U.S.S.R., France, and Italy. By applying the ratio of world-to-U.S. consumption for the period 1908–63 to the resource pool as developed for the United States, the secondary resource pool for the world is estimated to be approximately 90 million tons.

TABLE 3.—*Secondary copper produced in the United States*

[Short tons]

	1954–58 (average)	1959	1960	1961	1962	1963
Copper recovered as unalloyed copper	247,073	261,588	300,259	290,805	301,374	314,643
Copper recovered in alloys [1]	632,697	668,982	571,129	558,134	620,454	659,783
Total secondary copper	879,770	930,570	871,388	848,939	921,828	974,426
Source:						
New scrap	430,570	459,563	442,023	437,829	506,154	552,583
Old scrap	449,200	471,007	429,365	411,110	415,674	421,843
Percentage equivalent of domestic mine output	88	113	81	73	75	80

[1] Includes copper in chemicals, as follows: 1954–58 (average), 14,485; 1959, 10,061; 1960, 12,714; 1961, 10,708; 1962, 9,986; and 1963, 10,191.

RESERVES

Although the world is plentifully endowed with copper, the six principal producing areas contain 85 percent of the world measured and indicated reserve. In order of the magnitude of reserves these are the western slope of the Andes in Chile and Peru, the central African copper belt in Northern Rhodesia and the Republic of the Congo, the Western United States, the Ural Mountains and the Kazakstan region in the U.S.S.R., the Precambrian area of central Canada, and the Lake Superior region of North America. New discoveries and development of extensions of known deposits during the last decade increased the known copper resources. The measured and indicated world reserve, in terms of metal content, is estimated to be 212 million tons of copper. The estimates are based on the assumption that the cost price ratio will be such as to permit mining ore having approximately the same grade as that now being produced.

The reserves of selected countries are—

Country	*Ore reserves copper content (thousand short tons)*
Australia	1,200
Canada	8,400
Chile	46,000
Mainland China	3,000
Republic of the Congo	20,000
Japan	1,200
Peru	12,500
Republic of the Philippines	1,000
Poland	11,400
Northern Rhodesia	25,000
Spain	4,500
United States	32,500
U.S.S.R.	35,000
Yugoslavia	2,700

Reserves in Bolivia, Cuba, Cyprus, Finland, India, Mexico, Norway, Sweden, Turkey, and other countries total about 7.5 million tons. The extension of mine workings and delineation of new deposits by planned expansion and exploration projects will change substantial inferred reserves into measured and indicated ore.

An important part of the reserve is the ever-increasing reservoir of secondary copper which is being created and is capable of providing for about one-third of the Nation's requirement. There is no statistical series showing the amount of copper consumed in end-use items that would indicate the quantity in service in nondissipative use. However, assuming that three-fourths of the new copper is consumed in the manufacture of reclaimable products, it is estimated that the reserve of recoverable copper in use in the United States exceeds 35 million tons.

CONSERVATION

Mining and metallurgical research leading to more economic extraction and beneficiation of copper ores have made immense tonnages of ore available which otherwise would have been of no value as a source of copper. The need for lower costs, in turn, has encouraged research for the development of more efficient methods and techniques at all levels in the production of copper and copper products.

One of the most effective conservation practices is the reclamation of copper from scrap that provides approximately one-fourth of the U.S. supply. Another noteworthy conservation practice is the recovery by leaching of copper from material too low-grade or with a minera-

logical content unsuitable for concentration. Native copper is also recovered by reworking old tailing from gravity concentration, flotation, and leaching.

SOURCES OF STATISTICAL INFORMATION

Monthly and annual data on mine production of recoverable copper are reported by producers to the Federal Bureau of Mines; monthly data on production of blister copper, refined copper by shapes, stocks of blister, and refined and unrefined copper are reported by the primary smelting and refining companies. Primary copper plants and chemical establishments report stocks, production, consumption, and shipments of copper sulfate monthly, and copper smelters report production of byproduct sulfuric acid annually. Sales of copper by copper-selling agencies are reported annually.

Consumption of refined copper by major industry classes is reported monthly. Consumption of scrap by types, by primary copper producers, secondary smelters, and brass mills is reported monthly. Other consumption data collected annually include consumption of brass and bronze ingot by foundries, and refined copper and scrap at foundries, miscellaneous manufacturers, and chemical plants. The domestic data collected are sufficiently adequate and accurate for current programing and planning. However, data on consumption of copper by end uses and geographic locations are not available. Also, the Bureau of Mines does not gather data on consumption outside the United States.

World mine and smelter production data are compiled by the Bureau's Division of International Activities. U.S. imports and exports of copper are obtained by the Bureau of the Census.

Statistical information on world production and consumption is published by the American Bureau of Metal Statistics and the British Bureau of Nonferrous Metal Statistics.

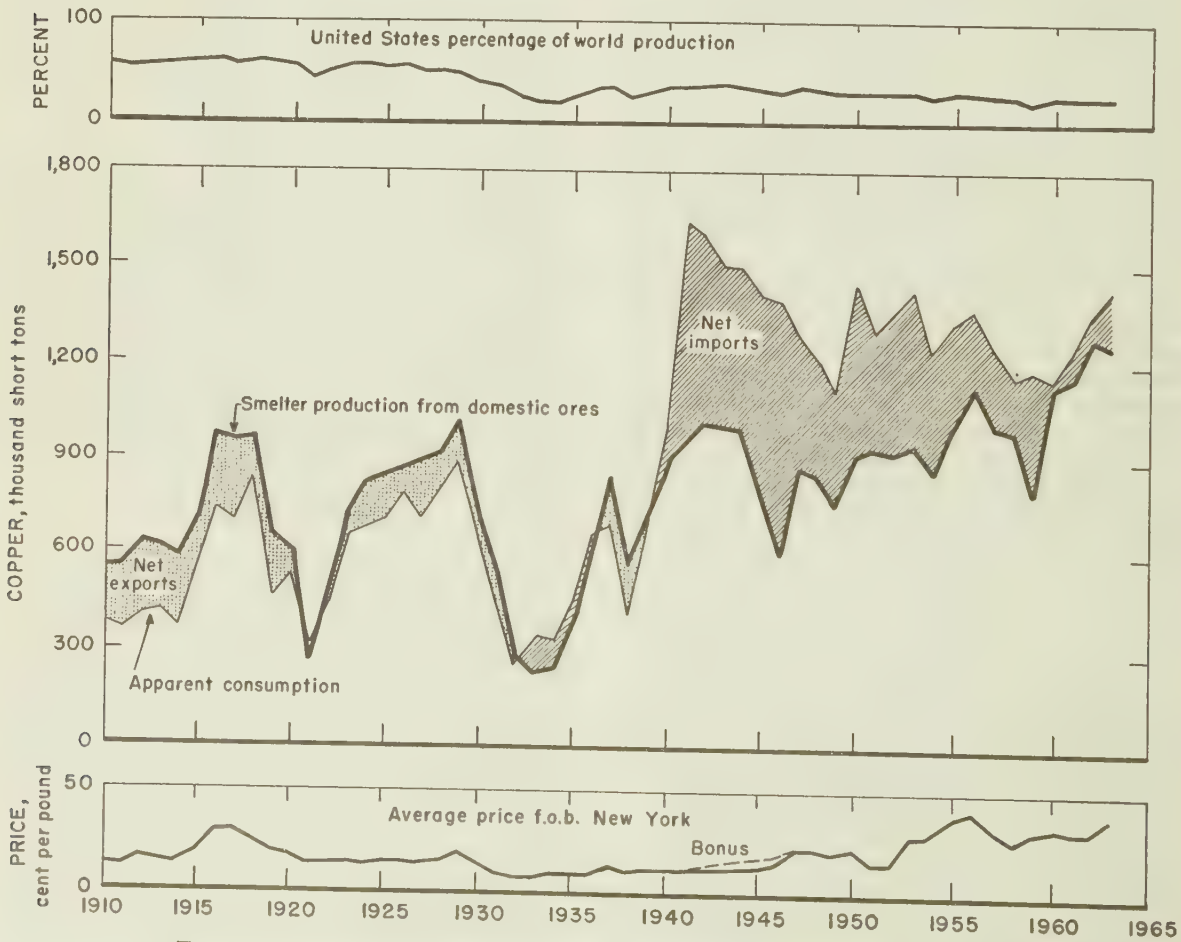

FIGURE 1.—Production, Consumption, and Price of Copper in the United States.

PRODUCTION, CONSUMPTION, AND TRADE

Production

World mine production of copper climbed steadily from 3.1 million tons in 1954 to a record of 5.2 million tons in 1963. The increased rates were attributed mainly to new properties attaining production schedules and established mines producing at accelerated rates, conditions that were encouraged by strong demand and high prices quite free from pronounced fluctuations.

The United States has been the largest copper-producing country for many years (figure 1). It lost this position only once since 1883, when Chile outranked it in 1934, a depression year. However, the percentage of world production produced in the United States has declined from about 52 percent in 1926 to 23 percent in 1963.

Consumption

Annual consumption of copper in the world increased from 4,369,000 tons in 1959 to 5,315,000 tons in 1963, an increase of about 22 percent, according to data compiled by the American Bureau of Metal Statistics. Comparable data for the previous 5-year period were 3,482,000 tons in 1954 and 4,075,000 tons in 1958, an increase of 17 percent. The rise in consumption in the last decade is attributed to growth of industry and electrification in developing nations and accelerated expansion of industrial activities in others. The United States continued to be the largest copper-consuming country in the world, accounting for about 30 percent of the total world consumption in 1963. Estimates of consumption in the U.S.S.R. placed it in second place in 1962 and 1963 with about 12 percent of the total for each year. Consumption of copper in the United Kingdom reached a high in 1960 when the country was in second place with about 13 percent of the total consumption. Thereafter consumption in the United Kingdom declined through 1962 and although use rose in 1963 the country remained in third place with less than 12 percent of the total. Use of copper in the Federal Republic of Germany reached a peak in 1961 when the country was in second place, consuming 12 percent of the world total. Thereafter use declined and by 1963, the country was in fourth place with about 10 percent of the total. Consumption increased in Japan by 40 percent from 1959 to 1963 and use rose about 30 percent in Canada during the same years.

Consumption of refined copper in the United States rose almost 20 percent from 1959 to 1963 when a record high of 1,744,000 tons were used. There are no recent continuing statistical data showing the consumption of copper by end uses. However, percentages of the total consumption in 1960 by industrial and other uses, prepared by a large producer of copper, are shown in table 2. The pattern of major uses of refined copper by broad industry classifications (table 8) remained virtually unchanged from 1959 to 1963. Average consumption for the 5 years at wire mills was 58 percent of the total and at brass mills was 39 percent.

Trade

The United States is the leading country in the world trade of copper. Crude materials, such as ores, concentrates, matte, and blister, as well as refined copper are imported. Refined copper and fabricated copper, fabricated-copper products, and manufactured goods containing copper are exported. The other leading producing countries—Canada, Chile, Northern Rhodesia, Peru, and the Congo (Léopoldville)—export most of their output. West Germany and the United Kingdom regularly import most of their requirements.

Except for a few years after World War I and during the depression of the thirties, U.S. production of copper exceeded domestic demand and there was a substantial surplus for export. World War II disturbed the balanced trade through which smelting, refining, and fabricating facilities of this country were used to treat foreign crude materials while refined copper and manufactures of the metal were returned abroad. After the beginning of the war, the United States needed all the copper produced in the country and imported it to fill the large armament requirements. The high level of industrial activity after the war continued to require large supplies of copper, much of which was met by importations. The alltime record high for imports was reached in 1945 when receipts of all unmanufactured copper totaled 853,000 tons and a record of quantity of refined copper (531,000 tons) was received. The outbreak of war in Korea in June 1950 again made large imports of copper necessary. Imports met about one-fourth of the U.S. requirements until 1959. Exports exceeded imports in 1960 for the first time in 20 years. The United States returned to a net importing nation in 1962 and this condition became even more pronounced in 1963. From 1959 through 1963, 44 percent of the imports of unmanufactured copper came from Chile and 19 percent from Canada. Imports from Peru averaged 15 percent of the 1959–63 total as a result of increased production in the country from 1959 onward.

TABLE 4.—*Supply and distribution of copper in the United States*

[Thousand short tons]

Year	Supply					Distribution			
	Production			Imports (refined)	Total	Consumption		Exports (refined)	Total
	Primary		Secondary (old scrap)			Refined	Secondary (in alloys)		
	Domestic materials	Foreign materials							
1954–58 (average)	994	366	449	180	1,989	1,376	324	274	1,974
1959	796	302	471	214	1,783	1,463	327	159	1,949
1960	1,121	398	429	143	2,091	1,350	270	434	2,054
1961	1,181	369	411	67	2,028	1,463	257	429	2,149
1962	1,214	398	416	99	2,127	1,600	253	337	2,190
1963	1,219	377	422	119	2,137	1,744	269	311	2,324

TABLE 5.—*Mine production of recoverable copper in the United States, by States*

[Short tons]

State	1954–58 (average)	1959	1960	1961	1962	1963
Alaska	2	36	41	92		
Arizona	467,927	430,297	538,605	587,053	644,242	660,977
California	706	663	1,087	1,382	1,162	916
Colorado	4,476	2,940	3,247	4,141	4,534	4,169
Idaho	6,972	8,713	4,208	4,328	3,861	4,172
Michigan	50,318	55,300	56,385	70,245	74,099	75,262
Missouri	1,714	1,065	1,087	1,479	2,752	1,816
Montana	83,902	65,911	91,972	104,000	94,021	79,762
Nevada	74,771	57,375	77,485	78,022	82,602	81,738
New Mexico	64,866	39,688	67,288	79,606	82,683	83,037
Pennsylvania [1]	8,602	6,604	7,908	8,934	6,108	4,435
Tennessee	9,669	11,490	12,723	12,272	14,298	13,717
Utah	224,486	144,715	218,049	213,534	218,018	203,095
Washington [2]	2,466	49	84	67	41	70
Total	1,000,877	824,846	1,080,169	1,165,155	1,228,421	1,213,166

[1] Includes North Carolina, South Dakota, and Vermont.
[2] Includes Oregon and Wyoming.

TABLE 6.—*World mine production of copper, by countries*

[Short tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963
Australia	62,292	106,344	122,567	107,102	123,849	128,185
Bulgaria	7,000	11,000	12,000	19,600	21,500	20,300
Canada	337,562	395,269	439,262	439,088	457,385	458,396
China	16,000	55,000	77,000	88,000	99,000	99,000
Chile	493,762	602,108	591,330	607,233	653,613	662,565
Congo (Léopoldville) [1]	261,404	310,955	333,175	325,402	325,442	297,540
Cyprus (exports)	35,204	39,979	39,096	31,586	27,734	29,000
Finland	26,103	32,400	31,100	37,500	38,700	37,400
Germany: East	20,300	20,800	20,900	27,600	28,100	30,900
India	8,752	8,929	9,700	9,700	10,913	11,034
Japan	83,985	93,970	98,307	106,273	114,221	117,968
Mexico	63,914	63,134	66,502	54,359	51,945	61,576
Norway	16,235	15,828	16,966	15,379	17,124	12,135
Peru	52,662	54,914	200,313	218,315	183,854	195,521
Philippines	32,228	54,587	48,513	57,182	60,327	70,201
Poland	7,200	9,900	11,600	12,900	15,100	14,600
Northern Rhodesia	440,174	598,835	635,326	633,139	619,856	648,239
Southern Rhodesia	3,013	12,016	15,128	15,243	15,146	18,489
South Africa, Republic of	50,541	54,066	50,847	51,743	45,638	60,793
South-West Africa	25,821	34,392	22,597	27,778	24,971	35,774
Spain	8,141	12,136	8,785	20,029	20,580	26,275
Sweden	18,131	19,079	19,265	20,047	21,054	21,000
Turkey	28,188	30,551	30,110	31,793	31,115	28,305
Uganda [1]	8,719	13,377	16,257	14,742	17,173	17,875
U.S.S.R. [1]	420,000	480,000	550,000	600,000	720,000	770,000
United States	1,000,877	824,846	1,080,169	1,165,155	1,228,421	1,213,166
Yugoslavia	35,261	38,141	36,682	41,787	57,008	68,446
Other countries	47,379	49,611	62,506	58,862	64,270	62,429
World total (estimate)	3,610,000	4,040,000	4,650,000	4,840,000	5,090,000	5,220,000

[1] Smelter production.

TABLE 7.—*World smelter production of copper, by countries*

[Short tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963
Australia	53,652	76,712	79,561	69,997	97,818	99,076
Austria	10,423	11,601	12,964	13,044	14,186	14,385
Bulgaria	4,916	12,236	17,747	20,834	21,385	22,622
Canada	304,720	365,366	417,029	406,359	382,502	378,911
Chile	461,556	570,593	556,464	578,068	614,235	613,977
China	16,000	88,000	110,000	110,000	110,000	110,000
Congo (Léopoldville)	261,184	310,955	333,175	325,402	325,442	297,540
Finland	27,048	35,941	34,140	37,800	37,400	41,664
Germany:						
East	28,100	33,000	35,000	35,000	35,000	38,600
West [1]	279,809	310,729	340,695	335,488	339,778	333,799
Japan	104,701	169,318	204,494	232,659	233,828	277,841
Mexico	55,914	61,105	64,861	52,498	50,177	60,005
Norway	16,636	21,218	23,825	24,218	21,051	19,734
Peru	37,517	38,024	181,650	200,699	164,920	173,471
Poland	17,953	19,127	23,961	24,504	26,608	32,665
Northern Rhodesia	424,742	595,094	625,942	627,144	603,783	634,946
Southern Rhodesia				12,915	13,599	16,187
South Africa, Republic of	48,590	53,843	50,847	57,562	50,905	60,085
South-West Africa					1,338	22,904
Spain	6,389	12,136	9,041	20,029	20,580	26,275
Sweden	19,999	27,922	23,927	22,822	25,098	25,000
Turkey	26,461	27,599	28,674	22,040	28,412	27,326
Uganda	6,886	13,377	16,257	14,742	17,173	17,875
U.S.S.R.	420,000	480,000	550,000	600,000	720,000	770,000
United States [2]	1,106,195	841,795	1,233,629	1,207,354	1,322,614	1,296,700
Yugoslavia	34,249	38,858	39,384	34,027	50,421	54,048
Other countries	17,888	22,030	26,053	26,132	31,224	29,911
World total (estimate)	3,790,000	4,240,000	5,040,000	5,110,000	5,360,000	5,500,000

[1] Includes scrap.
[2] Smelter output from domestic and foreign ores, exclusive of scrap. Production from domestic ores only, exclusive of scrap, was as follows: 1954–58 (average), 1,006,649 short tons; 1959, 799,329; 1960, 1,142,848; 1961, 1,162,480; 1962, 1,282,126; and 1963, 1,258,126.

TABLE 8.—*Refined copper consumed by classes of consumers in the United States*

[Short tons]

Year	Wire mills	Brass mills	Chemical plants	Secondary smelters	Foundries and miscellaneous	Total
1954–58 (average)	771,950	563,450	1,642	7,395	31,748	1,376,185
1959	836,177	584,100	794	8,111	33,849	1,463,031
1960	828,823	486,460	1,036	8,206	25,371	1,349,896
1961	823,799	599,765	1,269	9,504	28,493	1,462,830
1962	922,908	636,149	1,488	9,460	29,671	1,599,676
1963	1,036,162	673,907	1,238	3,652	29,314	1,744,273

Imports from the Republic of South Africa with 6 percent of the total exceeded those from both Mexico (5 percent) and the Rhodesia and Nyasaland (3 percent). Receipts of blister and other unrefined copper totaled 63 percent, refined copper 25 percent, and ore and concentrate 11 percent.

Most of the copper exported from the United States is refined copper and in advanced forms of manufacture, in which the copper content is not calculable. Exports of copper were under control from World War II until September 1956 because supplies in the United States were inadequate to fill requirements. After removal of restrictions on exports, shipments increased yearly (except for 1959) until 1960 when 510,000 tons were exported, only 5,000 tons less than the all time record in 1917. Exports declined annually after 1960 and 345,000 tons was shipped in 1963. Shipments of refined copper, the principal export class, in 1959–63 averaged 334,000 tons.

Much of the output of copper in Canada is exported in various forms and shipments of unmanufactured material totaled 316,000 tons in 1963. Japan received about 62 percent of the copper content in exported ores, concentrates, and matte; the United States and Norway each received about 17 percent. The United Kingdom and the United States received about 46 percent and 34 percent, respectively, of the 215,000 tons of ingots, bars, and billets exported in 1963. Much of the remainder was shipped to France, India, and West Germany.

Most of Chile's output is exported as refined and blister copper. The United States receives 40 percent of the exports, principally as blister copper; the United Kingdom imports 20 percent, about two-thirds of which is refined metal. Of the 188,300 tons of copper exported from Peru in 1962, 69 percent was blister copper, 22 percent refined, and 9 percent ore and concentrate. The United States received 41 percent

of the exports; the United Kingdom and West Germany each imported 18 percent.

More unwrought copper was exported from Northern Rhodesia than from any other country during 1959–63. Exports of refined and blister copper reached a peak of 633,300 tons in 1963. During the 5 years under review, the United Kingdom received most of the shipments and West Germany was in second place.

Belgium is the principal destination of copper exported from the Congo (Léopoldville). Substantial quantities were shipped to Beira and Lobito depots, but it is thought that most of this copper was shipped ultimately to Belgium.

Imports of all classes of copper are an important segment of the supply of Japan. Imports of ore and concentrate rose from 370,000 tons in 1959 to 623,000 tons in 1963, with receipts reported from 43 countries. Shipments from Canada rose from 15,000 tons to 234,000 tons and those from the Philippines averaged 194,000 tons for the 5 years. Receipts of unwrought copper increased from 15,900 tons in 1959 to 115,000 tons in 1961 and declined to 52,000 tons by 1963. A large percentage of the unwrought copper was received from the United States.

Tariff

An excise tax of 4 cents per pound was imposed on copper June 21, 1932. The Government was virtually the only importer in World War II, and during the period it held this position the tax was not applicable. The tax was reinstated for a very brief period, following which it was suspended by acts of Congress from April 30, 1947, to June 30, 1950. The suspended tax, meanwhile, was reduced as a result of the Trade Agreement negotiations at Geneva in 1947, to 2 cents per pound effective March 16, 1949. The 2-cent tax came into effect on July 1, 1950, but was suspended again on April 1, 1951. The law provided that the Tariff Commission must notify the President within 15 days after the end of any calendar

TABLE 9.—*Copper (unmanufactured) imported into the United States, in terms of copper content* [1]

[Short tons]

Class and country	1954–58 (average)	1959	1960	1961	1962	1963
Class:						
Ores and concentrates	110,257	72,641	75,518	45,788	42,917	48,638
Blister and other unrefined	277,592	277,997	303,422	340,795	332,321	369,807
Refined	179,983	214,058	142,709	66,855	98,820	119,165
Other	7,170	6,195	2,695	4,231	4,793	2,923
Total	575,002	570,891	524,344	457,669	478,851	540,533
Country:						
Belgium-Luxembourg	481	8,504	2,673			12,657
Canada	102,494	112,318	117,641	78,354	98,753	90,750
Chile	233,298	241,392	208,167	226,971	225,394	227,910
Germany, West	2,626	24,342	8,739	14		2
Mexico	50,295	29,493	22,656	20,963	23,779	22,344
Peru	33,694	28,725	91,624	90,435	72,133	99,726
Philippines	14,261	13,759	17,562	13,898	10,126	14,907
Rhodesia and Nyasaland	48,706	32,622	5,795	10	18,997	22,101
South Africa, Republic of	19,395	30,981	28,228	23,474	24,460	36,368
Other	69,752	48,755	21,259	3,550	5,209	13,768
Total	575,002	570,891	524,344	457,669	478,851	540,533

[1] Data are "general" imports; that is, they include copper imported for immediate consumption plus material entering the country under bond.

Source: Bureau of the Census.

TABLE 10.—*Exports of refined copper from the United States, by countries*

[Short tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963
Germany, West	42,998	38,524	105,998	77,352	67,353	69,227
Italy	23,596	15,234	61,459	63,047	54,314	56,239
India	7,095	922	5,258	12,022	65,124	55,540
France	62,022	42,567	56,866	60,306	39,044	38,039
United Kingdom	54,824	26,300	90,664	76,371	52,186	33,082
Japan	18,446	5,333	35,569	60,839	13,134	15,499
Netherlands	14,206	7,131	13,658	9,102	6,467	7,973
Brazil	12,782	4,972	14,892	20,288	4,765	5,117
Argentina	6,374	4,268	12,469	12,885	8,931	1,811
Other	31,610	13,687	36,929	36,506	25,207	28,952
Total	273,953	158,938	433,762	428,718	336,525	311,479

Source: Bureau of Census.

month in which the average price dropped below 24 cents per pound, delivered Connecticut Valley, and within 20 days thereafter the President would revoke the suspension. The suspension was extended each year until 1955 when it was extended to June 30, 1958. Meanwhile, at the June 1956 meetings in Geneva on General Agreements Tariffs and Trade (GATT), copper was subjected to certain concessions. The excise tax on copper metal, ores, and concentrates would drop 15 percent (5 percent for each of 3 years) if the tariff were reimposed and the price of copper was not below 24 cents per pound. For fiscal 1957, 1958, and 1959, the excise tax would be 1.9, 1.8, and 1.7 cents, respectively. The latter tax became effective July 1, 1958. As the price of copper was above 24 cents per pound from July 1958 through 1963, the 1.7-cent-per-pound excise tax was applicable to imported copper throughout this time.

STRATEGIC CONSIDERATIONS

Self-Sufficiency

Prior to 1940 the United States was a net exporter of copper. Since that time, because of World War II and postwar demands, a substantial portion of the Nation's copper supply has been imported except for the years 1958, 1960, and 1961. The largest quantities were imported during World War II, the peak year being 1945 when net imports reached 721,000 tons. From 1946 through 1956 copper in unmanufactured forms received from foreign sources ranged from 200,000 to 500,000 tons per year. In 1957 and 1958, demand and imports decreased. A prolonged strike in 1959 caused a substantial loss of domestic production and created the need for a larger quantity of net imports. In 1960 imports and exports were almost equal and in 1961 the United States again became a net exporter. The United States returned to a net importing nation in 1962 and net imports in 1963 totaled almost 200,000 tons.

For the short term, the U.S. position with respect to an adequate supply of copper is satisfactory. This outlook is supported by an estimated annual mine production capacity of 1.5 million tons of copper; vigorous exploration, development, and expansion programs for increasing the output; an annual availability from second sources (old scrap only) of from 450,000 to 500,000 tons; and a reserve of 1,122,000 tons of copper in the national stockpile. Furthermore, expansion of copper production in Canada, Chile, and Peru provides ample sources of imports in the Western Hemisphere. However, increasing competition by foreign interests for the world supply of copper is encroaching on the U.S. supply from these nations.

TABLE 11.—*United States mine production of copper, apparent consumption of new copper and excess consumption over production*

[Thousand short tons]

Period	Mine production	Apparent consumption (new)	Excess consumption over production
1920–29 (average)	7,299	6,499	[1] 800
1930–39 (average)	5,023	4,919	[1] 104
1940–49 (average)	8,796	13,642	4,846
1950	909	1,447	538
1951	928	1,304	376
1952	925	1,360	435
1953	926	1,435	509
1954	835	1,235	400
1955	999	1,336	337
1956	1,104	1,367	263
1957	1,087	1,239	152
1958	979	1,157	178
1959	825	1,183	358
1960	1,080	1,148	68
1961	1,165	1,237	72
1962	1,228	1,352	124
1963	1,213	1,423	210

[1] Production excess.

Stockpiling

Copper is stockpiled under the authorizations of several statutes. The Strategic and Critical Materials Stockpiling Act of 1946 (Public Law 520) (a revision of Public Law 117 passed by the 76th Congress in 1939), provides for the acquisition and retention of stocks of strategic and critical materials and to encourage the conservation and development of sources of these materials within the United States, and thereby decrease and prevent whenever possible a dangerous and costly dependence of the United States upon foreign nations for supplies of these materials in times of national emergency. The Defense Production Act of 1950 authorized the Government to encourage expansion of productive capacity and supply by purchasing materials for Government use or resale. The reserve thus accumulated is referred to as the "DPA" inventory or stockpile. The Supplemental Stockpile was authorized by the Agricultural Trade Development and Assistance Act of 1954 (Public Law 480, 83d Congress), and materials acquired by the Department of Agriculture in exchange for surplus agricultural commodities that deteriorate and are costly to store are placed in this inventory. The "CCC" (Commodity Credit Corporation) inventory is acquired by the Department of Agriculture by barter of surplus agricultural commodities. If there is no Government use for the material, they are required by law to be transferred to the supplemental stockpile.

The status of Government stocks of copper on June 30, 1964, in thousand short tons was:

Grade	Strategic stockpile	DPA	CCC	Supplemental	Total	Maximum objective
Stockpile grade	1,008	96	-------	11	1,115	775

Industry Concentration

Sixteen of the 25 leading copper-producing mines in the United States are in Arizona and together produced 54 percent of the domestic output in 1963. A mine in Utah produced 17 percent, mines in one district in Montana and another in New Mexico produced 6 percent and 7 percent, respectively. Nevada's contribution of 7 percent was divided between two districts, one in the eastern part of the State and the other in the western part. Michigan supplied about 6 percent of the total from two areas on the Upper Peninsula and Tennessee contributed 1 percent from one locality. The ore was processed by milling or leaching facilities near the mines and most of the products of these plants were smelted at nearby establishments. Of the 8,600,000 rated annual smelter charge capacity (ore plus flux), 47 percent is located at eight smelters in Arizona. A smelter in Utah represents 14 percent of the total capacity and a plant in Montana 12 percent. A smelter in Washington has 7 percent of the total and three smelters in Nevada, New Mexico, and Texas each have 5 percent. Smelters in Michigan contribute 2 percent as does one in New Jersey and a smelter in Tennessee accounts for 1 percent.

Electrolytic refineries in the United States have a rated annual capacity of 1.96 million tons, of which 59 percent is in five refineries situated on the eastern seaboard as follows, New Jersey 30 percent of the total, Maryland 20 percent, and New York 9 percent. Other States and percentages of capacity are: Texas, 15 percent; Utah, 11 percent; Montana, 8 percent; Washington, 5 percent; Arizona and Missouri, 1 percent each. Three refineries that have an annual rated capacity of 137,000 tons of Lake copper are located in Michigan. A refinery in New Jersey, which also produces electrolytic copper, has 53 percent of the annual capacity of the fire refining in the United States. A refinery in New Mexico has 34 percent of the capacity and another in Texas, 11 percent.

Vulnerability of Supply

Much of the world's supply of copper is produced in major producing areas affected by social and political instability. Furthermore, a large proportion of the copper is transported from the country of origin to areas of consumption over long sealanes sometimes linked with overland routes through other emerging nations. Historically, imports meet about one-fourth of the U.S. demand for copper. Chile and Peru supplied 59 percent of the imports in 1963 and a large percentage of the receipts was blister. This supply is made vulnerable by ocean transportation and more than 60 days are required for shipping and refining. About 15 percent of the imports came from Africa and about two-thirds of the receipts were blister. Because they are confronted with much longer overland and ocean supply lines, exports from Africa are relatively more vulnerable and the time consumed by shipments from the source to market is greater than for receipts from South America.

GOVERNMENT PROGRAMS

Under the Defense Production Act of 1950, as amended, various types of production expansion assistance were developed for copper—production loans, Government floor-price purchase contracts with escalation provisions, certificates of necessity permitting accelerated amortization of capital investment for income tax purposes, and exploration loans amounting to 50 percent of total costs repayable from eventual production. The San Manuel Copper Corp. and the White Pine Copper Co. started delivering their production to the Government under the Defense Materials Procurement Agency (DMPA) floor-price contracts in the last quarter of 1957 after the price of copper had fallen to 27 cents in September. Copper reserves were developed in several areas as a result of exploratory work under the Defense Minerals Exploration Administration (DMEA) program.

Other defense measures were establishment of ceiling prices of copper and copper alloys and strict export controls. Early in 1953 the situation had eased to the point where price controls and national and international allocations of copper were abandoned although military and Atomic Energy Commission needs were still to receive preferential treatment. Due to the continuing shortage of copper until the middle of 1956, quantity export controls were maintained on copper through the third quarter of 1956 and on copper scrap through the third quarter of 1957.

Effective November 10, 1958, copper items, including ores, concentrates, etc., refined copper, copper scrap, and copper-base scrap, were removed from the U.S. Department of Com-

merce positive list (requiring export licenses) and placed on the general list for export to all destinations except Hong Kong, Macao, and the Communist nations. Effective February 20, 1959, the U.S. Department of Commerce reimposed controls on all copper exports; shippers were required to declare destinations of all shipments except those to Canada.

Copper was removed July 1, 1962, from the list of materials eligible for assistance through OME in the financial risk of exploratory ventures judged capable of increasing the Nation's resources of selected minerals.

PRICES AND COSTS

Average annual copper prices in the United States have ranged from 5.67 cents per pound in 1932, the lowest on record, to a peak of 41.88 cents in 1956. Under price control during World War II and for a short period thereafter when the Government granted premiums on a quota system for copper production, February 1942 to June 1947, the average price including all premiums was 14.3 cents per pound. Government regulation of prices following the outbreak of war in Korea established a ceiling of 24.5 cents per pound on January 26, 1951, which lasted until copper prices were decontrolled February 25, 1953. Labor strikes in the latter half of 1954 and increasing consumption of copper both in the United States and Europe resulted in a shortage of copper, and the price rose continually reaching 46 cents per pound on February 21, 1956, the highest in 90 years. Supply surpassed demand in the United States early in 1956 and the first reduction in price in more than 2 years was made in July of that year. A continuing high rate of production and declining consumption resulted in increasing stocks and the price of copper declined gradually until it reached a low of 25 cents per pound in January 1958. The price was raised to 26½ cents in July and to 29 cents in October.

Primary producers' price for electrolytic copper delivered was established at 33 cents per pound in November 1959 and remained unchanged until October 1960. On that date, cumulative effects of increased output slackened demand and large consumer inventories caused a 3-cent-per-pound drop to 30 cents. The price of copper declined in early 1961 to 29 cents per pound but rose to 31 cents by the middle of May. Primary producers' price for copper remained unchanged at 31 cents per pound through 1963, the longest period of price stability except when under Government control.

Information on operational or overall costs per unit of production or of final product for mining, milling, smelting, refining, marketing, etc., is not readily available. Costs of producing copper in the free world vary widely from country to country and from mine to mine. A study by the Rhodesian Selection Trust Ltd., indicated the cost of producing electrolytic copper in 1955 in the Northern Rhodesian Copperbelt was over 19 cents per pound compared with an average of about 18.25 cents per pound within the United States. An analysis of 1956 production in the United States by The Anaconda Company showed that 13.9 percent cost 30 cents per pound or more, 22.6 percent 29 cents or more, and 33.1 percent 25 cents or more, leaving a balance of 66.9 percent produced under 25 cents per pound, but implying the overall average cost per pound of copper in the United States exceeded that of foreign production. Another statistical study arrived at a 5-year (1954–58) cost of approximately 25 cents per pound for seven domestic and foreign producing companies that accounted for 30 percent of the world's mine production. A more recent study indicated that the median cost for 1960–62 has been in the bracket of 17½ cents to 20 cents per pound, a rise of 2½ cents over costs in the 1950's.

TABLE 12.—*Average prices of electrolytic copper*

[Cents per pound]

Year	Domestic f.o.b. refinery [1]	Domestic f.o.b. refinery [2]	Domestic copper delivered
1959	30.82	31.182	30.7
1960	32.16	32.053	32.1
1961	30.14	29.921	30.0
1962	30.82	30.600	30.8
1963	30.82	30.600	30.8

[1] American Metal Market.
[2] E&MJ Metal and Mineral Markets.

TAXES

The Federal Government and a few of the State governments levy taxes on incomes of copper-producing corporations. In most States, property or ad valorem taxes on the value of mineral or surface facilities and severance taxes are levied to provide revenues for counties, municipalities, and school districts.

Corporations producing copper are subject to the corporate income tax rates which consist of a normal tax of 30 percent on the total amount of taxable income and a surtax of 22 percent on taxable income in excess of $25,000. Generally taxable income is gross income less the actual monetary costs of producing that income. However, the tax law contains several special provisions regarding income derived from mineral

deposits (natural resources). In recognition of the wasting character of mineral deposits, a special deduction, known as percentage depletion, is allowed which may have no relationship to actual costs. In addition, the tax law provides special treatment for certain capital expenses incurred in finding and preparing mineral deposits for production. Producers are granted a depletion allowance of 15 percent on domestic and foreign production.

Property tax base varies from State to State and in some instances it differs in certain sections of a State. The basis for taxation of property in some States is present worth, in others it is net proceeds, and a few States use both. In Michigan, mining plants and equipment are exempt from taxation but ore bodies are carefully appraised for present worth. In Tennessee only real estate and plant facilities are subject to property tax.

Severance taxes, like royalties, are based on gross production. A true severance tax is one measured by applying a specific rate per unit (ton, pound) to the total quantity produced. Four of the major copper-producing States are recorded as imposing severance taxes; however, Arizona's is classified as a sales tax, Montana's is called a mine metal license, and Utah's is known as an occupational tax. These all are collected whether or not a profit is realized from the operation of producing, and therefore are rightfully considered severance taxes. New Mexico levies a severance tax and a sales tax, which is essentially another severance tax.

EMPLOYMENT AND PRODUCTIVITY

Employment

The working force of the copper industry engaged in mining and beneficiating ores, smelting concentrates, and refining copper has remained relatively steady since World War II, averaging approximately 33,000 men annually and ranging from a low of 29,000 in 1946 to a high of 37,000 in 1956. The average number of men employed daily in 1963 was 29,600. About half were engaged in mining, one-sixth in milling, and a third in smelting and refining. This distribution has been fairly uniform throughout the postwar years with increases and decreases of employment in all operations following the accelerated or relaxed industrial activity of the country.

The years of highest employment at copper mines were 1916 and 1917, slightly more than 61,000 men mined a little over 1 million tons of recoverable copper in 1916 and just under 1 million tons in 1917. In 1929 it took 37,000 men to mine 1 million tons; in 1942, and 1943, 23,500; in 1956 and 1957, 18,000; and in 1963, 11,800. This decrease in employment requirements is due to the adoption of mass mining and milling methods which require fewer production workers. The widespread mechanization and large-scale operations have changed the number of men and the types of skills needed. Men now are trained for specific tasks and less dependence is placed on the worker's mining skills. Mining is directed and supervised by experienced foremen in accordance with plans prepared by technically trained mine superintendents and engineers. Mechanization has increased the demand for mechanics, enginemen, technicians, and operators of many kinds of machines while eliminating a large number of unskilled laborers.

Productivity

Over the last 50 years the annual rate of domestic mine production of copper has more than doubled and the ore mined per year increased almost fourfold, while man-hours assigned to copper mining has declined by two-thirds. In 1914, 103 million man-hours were required to produce 36 million tons of ore containing 574,000 tons of copper, whereas in 1963, 35 million man-hours produced 146 million tons of ore yielding 1.21 million tons of copper. Converting this information into productivity terms, 0.35 tons of ore and 11.1 pounds of metal were produced per man-hour in 1914 as compared with 4.17 tons of ore and 69.3 pounds of copper per man-hour in 1963. The rise in productivity is due to the greater proportion of copper ore mined by open pit and highly productive, large-scale underground methods plus technological advances in mining processes and equipment.

Productivity in ore concentration plants may be measured by man-hours of labor per ton of ore milled. In the last two decades the amount of ore milled increased 60 percent while the average number of men working daily decreased 27 percent. In 1944, 18 million man-hours were used while processing 86 million tons of ore from which 814,000 tons of copper were recovered, whereas in 1963, 12 million man-hours were required in concentrating 141 million tons of ore, yielding 1.02 million tons of copper. Converting this information to productivity terms, 4.8 tons of ore was processed and 90.0 pounds of copper was produced per man-hour in 1944 compared with 12.1 tons of ore and 174.3 pounds of metal in 1963. Significant proportions of the increased efficiencies at new and enlarged concentrators are due to technological advances made in new equipment and automation resulting in treatment of larger tonnages by fewer men.

Data are not readily available on productivity at smelters and refineries principally because the number of workers and man-hours are not reported separately for smelters and refineries. Employment and man-hours worked at these establishments are relatively consistant and changes in productivity are caused by varying production quantities. Foreign materials account for about 25 percent of refinery output but foreign ores are a small percentage of domestic smelter charges. Therefore, man-hours worked at smelters and refineries have been matched with smelter output from domestic ores for the following productivity expressions of pounds of copper per man-hour. In the last 20 years employment at smelters and refineries averaged 11,200 men with a low of 7,700 in 1944 and a high of 12,400 in 1947. An annual average of 28.8 million man-hours were expended in producing an average of 912,000 tons of copper. The average production of copper during the 20 years was 63.3 pounds of copper per man-hour, ranging from a low of 50.9 pounds in 1946 to a high of 93.8 pounds in 1959. Improvements in smelting and refining processes that have increased productivity at smelters and refineries in the last few years are elimination of roasting at some smelters; larger reverberatory furnaces; deoxidation of converter copper by gas; improved methods for casting anodes, wire bars, cakes, and billets; and continuous casting at refineries.

TRANSPORTATION

Ore from surface mines in the United States is transported to concentrators by captive or privately owned standard gage railroads, trucks of large capacity, skipways, conveyor belts, or combinations of these facilities. Large underground mines have highly developed transportation systems consisting of rail haulage and hoisting facilities or shuttle cars and conveyor belts. Transportation of concentrate to smelters is by conveyor if the smelter is near the concentrator, or by railroad and/or large capacity trucks to more distant reduction works. Where a refinery is near or integrated with a smelter, unrefined copper is moved for refining by rail or by other methods such as crane and ladle.

In Chile and Peru, concentrate is smelted near the concentrators or moved to smelters by railroad only or combined with aerial tramway or pipeline. Smelter and refinery products for export are transported by rail to ports not too distant. Steamship distances from Valparaiso (Chile) to New York, Liverpool, and Hamburg are 5,300, 8,300, and 8,900 miles, respectively. Copper exported from Chile and Peru accounts for most of that metal shipped through the Panama Canal. Overall shipments through the Panama Canal are as follows (in thousand tons):

Origin	Destination	1959	1960	1961	1962	1963
South America, west coast.	U.S. east coast:					
	Copper (metal).	221	248	280	309	268
	Ore	25	36	32	37	19
Do	Europe:					
	Copper (metal).	318	373	426	427	395
	Ore	92	53	62	54	107
U.S. west coast	Europe: Copper (metal).	27	16	56	48	40
West Indies	Asia: Ore	7	6	10	11	12

Note: Does not include small shipments of undifferentiated metals.

Copper is transported from the Congo (Léopoldville) over three routes. The route between Elisabethville and the port of Matadi is entirely within the nation. Shipments are by rail to Port Franqui on the Kasai River, thence by the Kasai and Congo Rivers to Léopoldville where they are transferred to a railroad connecting with Matadi. The other routes are by railroad through either Angola (Portuguese) to the port of Lobito or through Northern and Southern Rhodesia and Mozambique (Portuguese) to the ports of Beira or Lourenco Marques. Most of the copper exported from Northern Rhodesia is shipped over the same railroads to Lobito, Beira, or Lourenco Marques.

Approximate distances between some shipping points in Africa are:

From	To	Miles
Elisabethville, Congo (Léopoldville).	Port Franqui, Congo	900
	Beira, Mozambique	1,600
	Lourenco Marques, Mozambique.	1,612
	Lobito, Angola	1,309
Port Franqui, Congo (Léopoldville).	Léopoldville, Congo	500
Léopoldville, Congo (Léopoldville).	Matadi, Congo	300
N'dola, Northern Rhodesia	Beira, Mozambique	1,446
	Lourenco Marques, Mozambique.	1,478
	Lobito, Angola	1,449

RESEARCH

Tremendous reserves of copper have been developed in recent years by extensive exploration projects in all the major producing countries. As a result, ore reserves in the principal copper-producing areas today substantially exceed those in the past. The increase has resulted from exploring new discoveries, reappraising idle mining districts, and developing inferred extensions of known deposits. In-

tensive engineering and geologic investigations and exploratory drilling, often supplementing geochemical and geophysical surveys, were used when exploring the deposits. Results of these exploratory programs often are verified by underground work which also yields large samples for metallurgical testing. New techniques using statistical analyses and computer programs have been developed to evaluate the results of exploration.

Manufacturing companies have done much to improve efficiencies and control costs by developing more efficient earthmoving and transporting machines. Drilling procedures have been improved by studies of drilling techniques and sizes and spacing of blast-drill holes. Introduction of ammonium nitrate-fuel oil explosives (ANFO) contributed to a reduction of blasting costs.

Most segments of the industry have research facilities and men charged with experimentally investigating methods, technologies, and equipment in their particular field. These studies are supplemented by research programs of the Federal Government and institutions such as foundations, associations, and colleges or universities. Attention has been directed in mining to ground stabilization, open-pit design, and development of equipment and procedures for determining stress relief in rock as mining progresses. Refinements in concentration have resulted from continuous research in methods and equipment for crushing, grinding, classification, and flotation. Studies of the recovery of copper from refractory ores by roasting ore, halide salt, and carbonaceous material have yielded encouraging results. Application of biological science to extractive metallurgy has been investigated. Research has indicated that nonpyritic smelting of native copper is feasible by substitution of other sources of sulfur, such as gypsum, for pyrite. The fabricating industry is widening its market research activities in traditional fields as well as in new areas.

The Copper Development Association was organized in 1963 with a membership that included copper mining companies, smelting and refining firms, fabricating mills, and foundries. The new group assumed responsibility of practically all the activities of the Copper and Brass Research Association which ceased operation December 31, 1963.

OUTLOOK

Appraising the future of the copper industry on the basis of past and current activities, trends, and future plans, there will be adequate sources of ore, ample processing equipment, and copper should keep at least its share of the metal market. There is a slowly rising trend in world consumption principally because expanding electrification, increased use of copper in the construction industry, and efforts to accelerate progress in developing nations.

Many companies, at home and abroad, are actively exploring and developing new or additional sources and are expanding facilities to meet anticipated future requirements. It has been estimated that mine capacity in the United States will increase at slightly less than 2 percent to 1.6 million tons by 1968. Activities contributing to the increased production are expansion of facilities of The Anaconda Company at Butte, Montana; the Utah Copper Mine and Chino Divisions of the Kennecott Copper Corp.; the San Manuel Copper Corp.; and development of new mines by The Anaconda Company near Tucson, Ariz.; Calumet and Hecla, Inc., on the Upper Peninsula of Michigan; Duval Corp., near Kingman, Ariz.; and the United States Smelting, Refining and Mining Co., near Bayard, N. Mex. Kennecott Copper Corp. is intensively exploring a deposit in Alaska. Development of a mine in Maine will return New England to a copper-producing area, a position it held from colonial times until recently. World mine capacity will be increased an additional 400,000 tons by expansion of facilities at a number of mines in Canada and development of new ones, particularly in Ontario and British Columbia; expansion and developments in Chile; expansion of facilities at producing mines and the development of the Chambishi mine in Northern Rhodesia; development of the Palabora mine in the Republic of South Africa; and more modest expansions in Australia and the Philippines.

Consumption of copper in the United States has lagged behind the expansion of the national economy as measured by such indicators as the gross national product and the increase of population.

Reasons for the slower rate of growth of the copper industry are twofold, replacement in use by aluminum and to a certain extent by other materials in electrical power transmission and building construction, and less raw materials and more services are required to fulfill the needs of the complex society of modern America. Thus copper competes with other raw materials and vies with communications, education, medical care, recreation, transportation, and other services for its share of the money of the American consumers. For these reasons the

consumption in the United States is expected to increase at slightly less than half the rate of the increase of the gross national product. Based on historical averages the growth of the consumption of copper will be approximately 1.5 percent a year—a rate slightly less than that anticipated for the growth of population.

Rising standards of living and increasing populations in developing nations indicate that the growth of consumption of copper in the world in the next decade will approximate twice that of the United States. This projection is predicated on the assumption that adequate copper will be available at prices as competitive with aluminum and other substitute material as at present.

Imports of copper in ore, concentrate, and smelter products have been fairly constant and have averaged slightly less than 400,000 tons for the past 10 years. However, the imports may diminish in proportion to an increase in competitive buying by foreign interests and the rate by which currently planned new refineries in foreign countries are constructed.

Strong national strivings in South America and the emergence of new, unstable nations in Africa will continue to affect adversely the place of copper in international trade. Internal political and economic pressures will tend to maximize mine production of copper and cause construction of facilities that will affect smelting and to a greater extent refining in the United States. Since these developments will not be made by economic considerations, world production will tend to increase in a nonuniform manner disturbing trade patterns and sustaining an imbalance between supply and consumption.

Smelter capacity in the United States may increase in areas where mine production increases, but may decline where dependent on imports for feed. There is little indication that domestic refinery capacity will be expanded, in fact some refineries may experience difficulty in obtaining raw material.

Secondary copper recovery will vary roughly with the business cycle. Most of the fluctuation will be in the quantity of copper recovered from new scrap, which will range from 450,000 to 550,000 tons a year. Study of the past pattern of production from old scrap and consideration of limited generation of the material indicates that old scrap will contribute a fairly stable supply of about 450,000 tons of secondary copper annually.

PROBLEMS

The copper industry is confronted with technical and economic problems related to resources, mining, concentration, reduction, fabrication, uses, and prices.

A fundamental problem of the domestic industry is the assurance of a continuing supply which entails finding and developing new resources. Exploration is frequently so uncertain and so costly to pursue that it is considered excessively expensive by many. However, maintaining an adequate domestic supply is essential to offset drains of an expanding economy or interruption of foreign supply by adverse events. Worldwide aspects of the supply problem relate to political and social instability in some major copper producing areas; and the general geographic separation of the producing and consuming areas of the world.

A major problem of domestic mine production is related to rising costs and depletion of higher grade ore. In nearly all the available ores, the copper and byproduct minerals occur in a very small proportion of the mass of rock that must be mined and processed to recover them. Bulk handling of such low-yield materials is economic only under rigorously planned and supervised operations. Reliable determination of the size, configuration, mineral content, and rock properties of an ore body is a necessary and costly prerequisite. Preparing an ore body for mining by open-pit or caving methods requires a large initial expense in both money and time. As the depth of underground mining increases, hazards and costs multiply. In open-pit mining the ratio of waste removal to ore extraction increases geometrically with depth.

Concentration, like mining, has problems of efficiently handling bulk materials. Changes in character of mineralization require adjustments of concentration practices and may affect reduction capacities. Reduction is cumbersome, costly, and energy consuming. The affinity of copper for oxygen is such that each melting or casting step is attended by contamination by oxygen unless air is excluded from all molten faces.

The increasing importance of copper recovered from oxide ores by leaching or the segregation process illustrates a problem of material handling in metallurgy. Cement copper from leach solutions and flotation copper from the segregation process are of substantially higher grade than the sulfide concentrates. However, cement copper frequently is fed into the reverberatory furnace with the concentrate and flux to form matte of much lower copper content.

The lack of knowledge of the properties of high-purity copper and the alloys of copper with rare earth elements and rare metals impedes the search for new uses of copper. Incomplete thermodynamic data on the metal and its compounds limit development of new processes and uses.

Closely related to the problems of primary copper production are those of the essential secondary copper industry. Other problems include more widespread and effective methods of scrap collection; greater recovery of metals from scrap and waste material; and less costly methods of identifying, separating, and treating scrap.

One of the most challenging problems of the copper industry is preventing the loss of markets to aluminum, steel, plastic, and other materials and at the same time gain a proportionate share of an expanding market. Additional problems are unexpected price fluctuations, difficulty in predicting supply and demand patterns on which effective planning can be based, and competition between domestic and foreign segments of the industry.

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CORUNDUM AND EMERY

By Paul M. Ambrose [1]

CORUNDUM ore is mined mainly from shallow open-cut workings seldom exceeding 20 feet in depth. Screens and jigs, frequently operated by hand and supplemented by handpicking, are used when water is available; otherwise the ore is entirely handpicked. Emery is mined exclusively from open pits.

In 1963 about 2,000 short tons of abrasive-grade natural corundum mostly from Southern Rhodesia was imported into the United States and processed by one firm for sale principally to the optical industry. There was no domestic production.

About 7,000 short tons of emery is mined by two firms near Peekskill, N.Y., and 1,000 tons a year is imported from Greece and Turkey by two firms in Massachusetts. Virtually all the imported and a small portion of the domestic emery is used in abrasive paper and cloth and as a polishing grain; the remainder is used as a nonskid element in pavements and stairways.

Artificial abrasives, because they are harder and more uniform, have largely replaced corundum and, to a lesser extent, emery.

World reserves of corundum and emery are large in comparison to consumption. Domestic and Canadian occurrences of corundum are not presently commercial, and the domestic reserve of emery is small.

Demand for corundum is expected to continue as long as a sufficient supply is available at competitive prices. The demand for emery for abrasive application is expected to decline 300 tons to 500 tons per year; however, use of emery for nonskid flooring is expected to increase slightly.

Problems of the corundum and emery industries are related to the lack of definitive methods of comparing their abrasive properties with those of other materials. The dependence of the United States on foreign overseas sources of corundum may create problems of supply in wartime, and the lack of low-cost supplies of emery near major industrial areas other than New York may lead to substitution in some localities.

BACKGROUND

This chapter deals only with abrasive corundum and emery. Gem corundum, principally sapphire and ruby, is included in the "Gem Stones" chapter.

The development of the bonded grinding wheel during the 1860's created a demand for high-quality abrasives. To meet that demand, commercial corundum mining in the United States began at Corundum Hill, N.C., in 1871. Other major mines producing corundum were at Buck Creek, Clay County, and near Sapphire, Jackson County, N.C.; Laurel Creek, Raburn County, Ga.; and in Gallatin and Madison Counties, Mont. All have been inactive since 1906, except for short periods during World Wars I and II (*12*).[2]

The introduction of aluminum oxide (synthetic corundum) about 1900 reduced the importance of natural corundum and emery as abrasives in grinding wheels, abrasive cloth, and for polishing grain.

The abrasive qualities of emery from the Greek island of Naxos were known 2,000 years ago. Naxos and adjacent islands continue to produce an emery much favored in Europe for grinding wheels. About 100 years ago, emery from Turkey first entered the world market.

Emery mining in the United States began near Chester, Mass., in 1868; near Peekskill, N.Y., in 1883; and near Whittles, Va., in 1917. Emery is produced in New York by DeLuca Emery Mines and Di-Rubbo & Ellis from deposits near Peekskill, N.Y. In 1963 these firms produced about 6,732 tons, valued at $119,000. The Massachusetts mines closed in 1912, and the Virginia mines closed in 1923.

[1] Commodity specialist.
[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Abrasive-grade corundum from the Republic of South Africa and Southern Rhodesia is imported and processed by the American Abrasive Co. of Westfield, Mass. In 1963, 2,035 short tons of abrasive-grade corundum, valued at $51,334, was imported. The finished products are sold directly to the optical and grinding wheel industries.

Corundum also is produced in India, Malaysia, Nyasaland, and Mozambique. At one time the United States, Canada, and the Malagasy Republic were substantial producers. The U.S.S.R. has extensive deposits in the Ural Mountains and in Central Siberia, but its output does not enter foreign trade, and production data are lacking (*2*, *4*, *6*).

Emery is imported from Greece and Turkey by Washington Mills Abrasive Co., North Grafton, Mass., and by Hamilton Emery & Corundum Co., Chester, Mass. There were 10 manufacturers of emery paper and cloth in 6 States and 33 manufacturers of bonded emery abrasives in 11 States. In 1963 these firms produced 74,018 reams of emery paper and cloth, valued at $2,670,165. This was about 3 percent of the coated abrasives, including quartzite, garnet, aluminum oxide, and silicon carbide sold that year.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Corundum is a natural anhydrous aluminum oxide. In its purest form it includes various gem stones, such as ruby (red) and sapphire (blue, yellow, green, purple, and white). Emery is a mixture of corundum, magnetite, and other minerals. It contains from 55 to 75 percent aluminum oxide, commonly in the form of fine crystals of corundum. Three commercial types of emery are recognized in the United States—Greek, Turkish, and American. The American type, from Peekskill, N.Y., is spinel emery, a mixture of spinel, corundum, and magnetite. The abrasive efficiency of each is normally determined by the percentage of included alumina.

Typical partial analyses of emery types are as follows:

Type	Alumina (percent)	Silica (percent)	Magnetic iron oxide (percent)
Turkish	62	2	33
Greek	63	5	29
American	55	7	30

National Stockpile Specification P–18–R, of November 28, 1961, covers two grades of corundum ore.

TECHNOLOGY

Significant Properties

On Mohs' scale the hardness of corundum is 9. The artificial abrasives—aluminum oxide and silicon carbide—have a Mohs' scale hardness slightly above 9 and emery has a rating of 8 to 8.5. The specific gravity of both corundum and emery is about 4. On the Wooddell and Knoop scales of comparative hardness, based on actual working conditions (*13*), the artificial abrasives are rated considerably harder than corundum. Because they are harder and of more uniform quality, artificial abrasives have displaced corundum, and to a lesser extent emery, in industry, except for a few special operations.

Corundum suitable for abrasive purposes has a prominent basal cleavage that causes the crystals to break readily with smooth flat surfaces at right angles to the axis of elongation through successive reductions in size. In this respect it differs from aluminum oxide, which has a conchoidal fracture. The difference in type of fracture may explain why corundum seems to be particularly suited for certain kinds of grinding.

Geology

Corundum occurs as a constituent of various igneous and some metamorphic rocks, including serpentine, mica schist, quartz schist, and crystalline limestone, and in contact metamorphic zones. Corundum also occurs in alluvial deposits.

In Africa corundum usually occurs in one of three forms: (a) Crystal corundum, comprising loose or isolated crystals derived from pegmatitic intrusions in decomposed or partly decomposed country rocks, generally basic in character; (b) boulder corundum, or detached rounded masses of corundum-bearing rock that have resisted disintegration. The boulders are usually composed of interlocking crystals of corundum, with lesser amounts of feldspar, mica, and other associated minerals filling the interstices; and (c) reef corundum, lenticular masses of rock locally called "plumasite," composed largely of corundum and a white acid-type plagioclase feldspar (*6*).

Emery deposits are products of contact or regional metamorphism. On the island of Naxos, which is principally made up of gneisses and mica schists, alternating with crystalline limestone, masses of emery from 15 to 50

feet wide and up to 300 feet long are closely associated with the limestone (*2*).

In Turkey, the deposits occur as pockets or masses in limestone, and range from a few feet to 200 feet in width and up to 300 feet in length. Emery occurs also as detritus resulting from the weathering of the rocks, and in a compact red clay which occurs in shallow depressions in the limestone (*2*).

Near Peekskill, Weschester County, N.Y., emery deposits occur on the border of an igneous complex composed of hornblende and olivine pyroxenite. The ore is a black or gray, massive, hard, fine-granular spinel emery (*3*).

Mining and Milling

In general, corundum is mined from shallow open-cut workings which seldom go deeper than 20 feet. In past years, some workings reached a depth of 100 feet. Few of the operations are mechanized (*7*). In the residual deposits crystal corundum is generally clean and free from adhering impurities, and the problem of recovery is to separate the crystals from the accompanying waste. Usually the ore is screened to minus 1- plus ⅛-inch, and washed in a rotary pan similar to that used for the recovery of diamonds, or in small jigs, often operated by hand. The larger crystals and fragments can usually be recognized during the screening and are picked out by hand. If water is not available for washing, the material is hand-picked. No effort is made to recover the minus ⅛-inch material (*11*). The massive corundum deposits in Southern Rhodesia are mined by open-pit methods, and the ore is handpicked and shipped in bulk.

All producing emery mines in the United States, Greece, and Turkey are open pits.

USES

Corundum and emery are used as abrasive components of grinding wheels and abrasive cloth or for polishing grain. Their use has been virtually supplanted by artificial abrasives, and less than 4 percent of the abrasive material now used is corundum or emery.

Corundum is used in the rough and finish grinding of optical glass. For rough optical grinding, corundum grain from 60- to 275-mesh is employed. As the corundum grain breaks down it is collected with the powdered glass it has abraded. This material is treated by water classification to produce superfine corundum for finish grinding of optical glass (*8*). A grade of corundum not suitable for abrasive purposes is used locally in Southern Rhodesia for refractories.

Turkish emery is preferred by industry over other types for abrasive paper and cloth and in recent years the combined sales of emery paper and cloth have been about 3 percent of the total coated abrasives sold. Emery is also used in lapping and polishing compounds, and for polishing grain. During the last decade, domestic emery has been used as a nonskid element in pavements and stairways, and this is now its largest use. The low price of domestic emery in comparison with other abrasives is a factor in expanding this use (*5*).

ALTERNATE MATERIALS

Aluminum oxide, made principally from abrasive-grade bauxite, and partly from Bayer process alumina, has largely replaced corundum and emery in grinding and polishing operations. Some garnet is used in optical lens grinding. Corundum and emery still are used in a few applications either because of price, performance, or preference. Examples are the use of corundum for lens grinding and emery for metal polishing. To a lesser extent, silicon carbide has also become competitive as the abrasive element in grinding compounds.

Among the natural abrasives, diamond, because of its extreme hardness, and garnet, because of its unique fracture, also have replaced corundum and emery for some uses.

Corundum and emery formerly were used for sandblasting and sandpaper to a limited extent, but have been replaced almost entirely in these uses by lower priced sand and quartzite.

RESERVES

The Republic of South Africa, Southern Rhodesia, and India have corundum deposits occurring over large areas. No reserve data are available, but it seems probable that the present corundum output can be maintained for the foreseeable future. Nyasaland, Mozambique, and Malagasy Republic have substantial deposits, and corundum is known to occur in several other countries, including Brazil and Malaysia. There is no reserve of corundum in the United States or in Canada. The U.S.S.R. may have the largest reserve of corundum in the world in the Ural Mountains and in Central Siberia.

A study of the emery deposits near Peekskill, N.Y., made by the Bureau of Mines in 1955, indicated a reserve of some 60,000 tons of emery. The potential resource is many times the indicated reserve. The emery deposits near Chester, Mass., have not been worked since 1913, and those in Virginia for over 30 years. Emery occurrences are known in Pennsylvania and

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North Carolina. No estimates of the ore reserves at these locations are available.

Greek and Turkish emery deposits have reserves reported as "large," and it seems probable that their present output can continue for many years. With mechanization, and possibly beneficiation, these areas can probably increase their emery output, lower costs, and improve the product. Emery from U.S.S.R. deposits does not enter free world trade. The total reserve is reported to be large. Canada has no known commercial deposits. Minor reserves are known in Bavaria.

SOURCES OF STATISTICAL INFORMATION

The Bureau of Mines annually compiles data on the world corundum production and canvasses the domestic emery producers. The Department of State reports information on the production of emery in Greece and Turkey.

PRODUCTION, CONSUMPTION, AND TRADE

The world production of corundum and emery, by countries, is shown in tables 1 and 2; imports into the United States are shown in tables 3 and 4. It is estimated that more than one-half of the emery consumption in the United States is used for nonskid floors and pavements.

There is no duty on corundum ore and concentrate. The import duty on graded corundum is one-half cent a pound. There is no duty on emery.

TABLE 1.—*World production of corundum by countries* [1] [2]

[Short tons]

Country [1]	1954–58 (average)	1959	1960	1961	1962	1963
Argentina	6					
Australia	2					
India	424	236	276	363	332	[3] 330
Malaysia	[4] 21					
Mozambique	2					
Nyasaland	8					
Southern Rhodesia	3,511	2,799	3,843	2,792	3,348	5,941
South Africa, Republic of	1,601	622	123	159	349	65
World total (estimate) [1] [2]	10,000	8,000	9,000	8,000	9,000	11,000

[1] Corundum is produced in U.S.S.R., data on production are not available, and estimate is included in the total.
[2] This table incorporates some revisions. Data do not add exactly to totals shown because of rounding where estimated figures are included in the detail.
[3] Estimate.
[4] Exports.

TABLE 2.—*World production of emery*

[Short tons]

Year	United States	Turkey	Greece	Total [1]
1954–58 (average)	10,445	5,686	8,420	24,551
1959	8,555	5,323	7,716	21,594
1960	8,169	7,511	7,716	23,396
1961	6,180	9,179	7,937	23,296
1962	4,316	3,757	8,377	16,455
1963	6,732	8,256	8,267	23,255

[1] Excludes U.S.S.R. production.

TABLE 3.—*U.S. imports of corundum ore*

Year	Quantity (short tons)	Value
1954–58 (average)	2,631	$134,487
1959	3,335	125,954
1960	2,654	77,243
1961	2,396	54,856
1962	2,430	57,326
1963	2,035	51,334

TABLE 4.—*U.S. imports of emery ore*

Year	Short tons	Value
1954–58 (average)	941	$15,020
1959	1,120	13,500
1960		
1961	1,120	10,000
1962	2,240	19,500
1963 [1]	560	13,000

[1] Not separately classified beginning Sept. 1, 1963.

STRATEGIC CONSIDERATIONS AND GOVERNMENT PROGRAMS

The Western Hemisphere has no commercial corundum deposits, but artificial abrasives can replace corundum for all uses, although at a higher cost and some undetermined loss in efficiency in certain operations.

The emery resources near Peekskill, N.Y., probably are adequate for many years, and the product is acceptable for the domestic market both in quality and price. Only a few consumers feel that they must have imported emery, and in time of shortage, artificial abrasives can probably be substituted for emery without much loss of efficiency.

Consumers of corundum and emery are concentrated in the northeastern section of the United States (*9*).

Corundum is included in the list of strategic and critical materials for stockpiling, principally because of its use in lens grinding. On June 30, 1964, government inventories totaled 2,008 tons of corundum ore, all of which was in the national (strategic) stockpile. The maximum objective was 2,500 short dry tons.

PRICES

Water classified corundum optical powders ranged from $0.34 to $1.12 per pound according to the fineness of the product. The availability of finer powders between 1959 and 1963 was largely responsible for the increase from $0.63 per pound for the finest size in 1959 to $1.12 for the finest size in 1963.

Emery from Turkey and Greece was quoted at 11 to 14 cents a pound, depending on particle size, compared with 8 cents a pound for equivalent domestic emery in 350 pound bags. Domestic emery aggregate for use in nonskid floorings was quoted at 8 to 11 cents a pound for graded sizes in quantities of 25 short tons, packed in 100-pound paper bags.

TAXES

There are no special taxes on the corundum or emery industries. Producers of corundum are granted a depletion allowance of 23 percent on domestic and 15 percent on foreign production. Producers of emery are granted a depletion allowance of 15 percent on both domestic and foreign production.

TRANSPORTATION

Transportation costs on corundum from the African mines to Westfield, Mass., total about $35 a short ton. Ocean freight from Turkish or Greek ports to New York or Boston on emery ore ranges from $10.00 to $12.50 a metric ton.

RESEARCH

Practical techniques for evaluating natural corundum have been developed by the National Bureau of Standards (*1*). Private industry has made some studies on the use of emery for nonskid pavements and airport runways. Since 1952 the Federal Bureau of Mines has conducted continuing research on techniques for production, fabrication, and testing of numerous metallic borides, carbides, nitrides, and silicides. Some of these compounds may develop into suitable replacements for corundum and emery.

OUTLOOK

For certain specialized abrasive uses, corundum probably will continue to be in demand as long as a sufficient supply is available at comparable prices.

Consumption of corundum in the United States is expected to remain fairly constant at the rate of about 2,500 tons per year for several years. Its use in optical grinding should increase slightly, while other uses decline because of competition from manufactured abrasives, particularly aluminum oxide.

The use of emery in abrasive products, which has declined at an average rate of over 500 tons per year for the past 10 years, is expected to continue to decline, but at a lower rate. Emery for nonabrasive applications, principally nonskid concrete surfacing, should remain fairly constant with possibly a slight upward trend because of use in nonskid paving.

Resources of foreign corundum and emery, and domestic emery are believed to be adequate for the forseeable future although quantitative data are not available.

Competition from other abrasive materials, particularly artificial abrasives and industrial diamond, will be keen due to continuing product improvements, standardization of quality, and utilization research conducted by the abrasives manufacturers, processors, and distributors.

PROBLEMS

Corundum and emery share the overall problem of the abrasive industry; namely, a lack of definitive methods of evaluating the comparative abrasive properties of the various minerals and materials. Hardness, per se, does not assure that a material will be a good abrasive. Other factors, including type of fracture, crystal form, friability, and ability to withstand heating also determine abrasive value. Consequently, personal preference and price usually dictate the choice of abrasives.

Lack of adequate data on the relative grinding efficiency of corundum and emery versus the major abrasive products, aluminum oxide, silicon carbide, and diamond, makes it difficult for corundum and emery to compete most effectively in the relatively few areas where they have a real advantage on the basis of cost or product quality.

A major national problem is the lack of known commercial deposits of high-quality corundum in the United States for use in the event foreign supplies become unavailable.

The major problem of mines producing abrasive-grade emery is to maintain production at a profitable level while demand is decreasing because of competition from manufactured abrasives, labor costs are rising, and the ratio of waste rock to ore is increasing.

Domestic sources of emery are remote from major consuming areas other than the Northeastern States. This factor encourages the use of lower cost but less efficient local abrasive materials or more expensive abrasives which have longer service life and lower maintenance requirements to compensate for high transportation costs.

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DIAMOND—INDUSTRIAL

By Paul M. Ambrose [1]

THE WORLD is dependent on natural diamond for industrial stones but if required, necessary crushing bort and powder could be manufactured by processes similar to the one developed in 1955. Natural diamond is available mainly from Africa. Manufactured diamond, first available in the United States, now is produced in five other countries.

"Industrial Diamond, A Materials Survey," was prepared by the Bureau of Mines under the sponsorship of the Office of Emergency Planning to provide comprehensive, fundamental information on diamond essential to the national security. This information circular contains pertinent information on occurrence, technology, production, imports, consumption, exports and history usually in some detail and occasionally back to 1900 (*5*).[2]

Substantial demand for industrial diamond began with the development of hard materials, such as tungsten carbide, and the need for an abrasive to grind and polish them. This created an expanding market for industrial diamond material unsuited for gems, which formerly was difficult to sell. World production of industrial diamond reached 30 million carats in 1963, worth about $120 million. The Congo (Leopoldville) was the largest source.

The principal primary source of diamond is believed to be kimberlite, which occurs in the form of pipes, dikes or sills. Placer deposits derived from the erosion of the original diamondiferous rocks are a more important source of industrial diamond material, supplying over 90 percent of the world output.

The largest outlet for industrial diamond is in the manufacture of abrasive grinding wheels. Industrial diamond also is used in grinding wheel truing and dressing tools; in core, oil well, and blasthole drill bits; lathe tools; wire drawing dies; and hardness indenters. In addition, whole diamonds and crushed bort are used in diamond saws, and diamond powder is used to polish metal parts and jewel bearings.

Several cutting or shaping techniques other than grinding have been developed to reduce the use of industrial diamond, some of which have proved competitive. Their application in industry is, to some extent, dependent on the availability and price of industrial diamond.

Manufactured diamond, produced by General Electric Co., has proved a satisfactory abrasive and makes the United States less dependent on African sources of industrial diamond. Manufactured diamond also is produced in Ireland, Japan, the Republic of South Africa, Sweden, and U.S.S.R.

The world reserve of industrial diamond is estimated to be about 600 million carats, of which 99 percent is in Africa.

Research directed toward the improvement of diamond wheel manufacture and operation and the setting of diamonds in core and oil well bits has improved the quality and quantity of work done.

Since 1946 the Bureau of Mines has conducted research on hard materials and abrasives that may be substituted for diamond in certain applications.

Large reserves of natural diamond in Africa, manufactured material, and the salvage of diamond from industrial wastes give the users of industrial diamond an assurance of supply that should greatly encourage its use. With competition entering the supply field, the possibility of lower prices is an added stimulant.

Major problems of the abrasive industry include a lack of low-cost effective substitutes for industrial diamond, the need for definitive methods of evaluating its abrasive qualities, and a lack of data on consumption.

[1] Commodity specialist.
[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

BACKGROUND

Probably the first industrial use of diamond was in the form of diamond powder for polishing gem diamonds and other precious stones. Diamond from the early discoveries in India, Borneo, and Brazil found little industrial use. As early as 1819 a patent had been issued in England for drawing wire through a diamond die and glass cutting was an important early use for diamond.

The discovery of the South African diamond mines in 1867 filled the market with industrial material and provided an ample supply for diamond drill bits and grinding wheel truing and dressing tools.

Diamond grinding wheels became important during World War I when German inventors introduced cemented-carbine cutting tools. Grinding wheel manufacturers are now the largest users of industrial diamond.

Prior to World War II the supply of industrial diamond far exceeded the demand. Before 1939 nearly 124 million carats of industrial diamond had been mined, 52 million carats had been used by industry, and there was an apparent surplus of 70 million carats. Between 1940 and 1945 the visible supply was reduced 33 million carats and between 1946 and 1960 it was reduced another 42 million carats. Increased use of diamond and stockpiling has resulted in a nearer balance between supply and demand.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Extensive use of diamond by industry dates only from shortly before World War II (*8, 9, 19*). From 1936 to 1956 imports of industrial diamond into the United States rose from about 1 million carats to 16 million carats valued at nearly $75 million, mainly because of the adoption of cemented-carbide cutting tools by the metal-cutting industry. In 1963 imports were 12 million carats valued at $50 million.

Africa produces about 90 percent of the world supply of natural industrial diamond, U.S.S.R. 9 percent, and South America less than 1 percent. In 1963 the Congo (Leopoldville) produced 66 percent of the total world production; followed by Ghana, 7 percent; Republic of South Africa, 9 percent; and Sierra Leone, 3 percent. Seven other countries account for the rest of the African output.

Most of the world natural diamond sales are made through the Central Selling Organization which is made up of Diamond Corp., Ltd., The Diamond Purchasing and Trading Corp., Ltd., The Diamond Trading Co., Ltd., Industrial Distributors Ltd., and the Diamond Development Co., Ltd. Another organization, Diamond Producers Association, has great enough influence over the combined group to make it possible for minority interests to be heard (*5*, p. 100, 107–112), (*24*).

The industrial diamond product manufacturers in the United States are centered largely in the Northeastern States, with a few firms in the Los Angeles, Calif., area and in the Midwest.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

All diamond material is suitable for industrial use, but some, because of its color, structure, or size, is more valuable for gem purposes. Gem diamond is discussed in the Gem Stones chapter. Industrial diamond is classified usually according to its potential use into *industrial stones*, such as: Die stones (for wire drawing dies); tool stones (for shaped tools, hardness indentors, etc.); dresser stones (for truing grinding wheels and tools); and drilling stones (for core and blasthole drilling, stone saws, etc.); and *bort* (usually fragmented, for use in making grinding wheels, saws, impregnated core drill bits, and diamond powders).

These classifications are subdivided according to quality, size, crystal habit, and color into over 100 groups. Classification and grading of industrial diamond are strongly influenced by the personal factor and require much skill and training (*28*).

The standard carat in use is the "metric carat" weighing 200 milligrams. It was adopted by international agreement in 1913 and was legalized in the Republic of South Africa in 1922. A previously used "Board of Trade" carat weighed 205 milligrams. Using the standard carat, 2,268 carats weigh 1 pound, and 5,000 carats weigh 1 kilogram. A common system of designating the weight of individual stones is the point system, wherein 100 points equals 1 carat. Smaller sizes are usually classified by passing them through screens. Diamond smaller than 60-mesh may be called "sand," "powder," or "dust" based on progressively decreasing size.

Dana, Bauer, and other authorities state that bort (also spelled boart, bortz) is a cryptocrystalline aggregate of diamonds, but the term is often used by the trade to mean any diamond material that is not of gem quality. Also the terms "common goods," "rejections," and "rubbish" are applied to the less desirable diamond material used for industrial purposes.

Machine shop waste containing diamond from grinding operations is called "sludge" if it is obtained from wet-grinding and "swarf" if obtained from dry-grinding.

The Bureau of the Census has adopted the following designations for the various classifications of industrial diamond imported into the United States: Miners diamond; crushing bort; powder or dust; other, not advanced in condition or value; other, advanced in condition or value; and synthetic.

TECHNOLOGY

Geology

Economically minable diamond occurs in kimberlite pipes, dikes, and sills, and in placer deposits. Over 90 percent of the world output of industrial diamond is from placer deposits.

Geological evidence indicates that diamond was formed in the kimberlite. The fact that diamond is not present in the majority of the known kimberlite occurrences throughout the world indicates that the exact conditions requisite for its formation were not present everywhere.

Although the kimberlite pipes in the vicinity of Kimberley, South Africa, showed practically no surface enrichment, other occurrences, such as the Premier mine in the Transvaal and the Williamson mine in Tanganyika, had a marked concentration of diamond near the surface.

Of the 150 kimberlite pipes and dikes discovered so far in South Africa, 16 have been worked for diamond, and only 11 have proved profitable (*33*).

The numerical ratio of profitable to unprofitable or barren occurrences of kimberlite, in any particular area, affords an indication of the likelihood of a new discovery of economic importance. Within a radius of 15 miles of Kimberley, Republic of South Africa, the ratio is one commercial mine to three barren kimberlite pipes. In the Jagersfontein area, Republic of South Africa, the ratio is 1:6 and in the Premier area, 1:10. In the vicinity of the Williamson mine, Tanganyika, the ratio is 1:26. None of the kimberlite occurrences in the Congo (Leopoldville), outside the Bakwanga area, has proved rich enough to work.

Commercial deposits in 1958 included six kimberlite pipe deposits—three near Kimberley, one at Jagersfontein, and one near Pretoria, Republic of South Africa (Premier mine), and one at the Williamson mine in Tanganyika—a kimberlite sill in Congo (Leopoldville), at Bakwanga, and a kimberlite dike in the Republic of South Africa, at Mallin.

The diamond-bearing ore at the Kimberley mine persisted to a depth of at least 3,500 feet, and at that point the yield was somewhat better than at the 2,500-foot level. However, rising mining costs caused the suspension of mining operations. Outside the Kimberley area, commercial values have seldom been found to continue over a large vertical range (*33*).

Diamond placer deposits are derived from the erosion of kimberlite or from the reconcentration of older placers. They range in age from Precambrian to Quaternary.

In South-West Africa and the adjoining areas of Cape Colony diamond is found in old beach lines as much as 100 feet above the present sea level. Diamond is also found in waters off the coast of South-West Africa.

The alluvial deposits now being worked in Sierra Leone, Guinea, Ghana, Congo (Leopoldville), and Angola are of recent age. They occur in stream gravels and bench deposits. Except for a kimberlite sill at the Bakwanga mine in Congo (Leopoldville), the source of diamond has not been found.

In the Lichtenburg diamond field in the Transvaal the diamonds are in the channels of an old river system. The diamonds in South America, Australia, Borneo, and India are in recent stream gravels.

In the United States diamond occurs in minor quantities in the detrital cover of a kimberlite pipe in Pike County, Ark. (*27*). Diamond has been found in glacial drift in Wisconsin, Michigan, Indiana, and Ohio and in placer gold workings in California and Montana. Individual diamonds have been picked up in 10 other States.

In 1956 a Russian geological expedition announced the discovery of diamondiferous kimberlite pipes, culminating a 6-year search for diamonds in Central Siberia. The principal field is in the basin of the Vilyui River in the northwestern part of the Yakutian A.S.S.R. Another field, 400 miles distant, is in the basin of the Daaldyn River. So far, no information indicating the definite extent of these discoveries has been published, but production of diamond by the U.S.S.R. in 1963 was estimated at 3 million carats of which 2.76 million carats was industrial diamond.

Mining and Milling

At the Premier and Jagersfontein mines and the mines at Kimberley the kimberlite pipes are mined underground by caving. The kimberlite, after crushing, is concentrated by heavy medium, followed by jigs, grease belts, and electrostatic separators, sometimes supplemented by handpicking (*13*). The ore contains about 1 part of diamond to 15 million parts of waste.

At the Bakwanga mine in the Congo (Leo-

poldville) the overburden is removed with continuous bucket excavators of German design. Mining of the diamond-bearing material is done with power shovels. The ore is treated by the same methods as that from the pipe mines in the Republic of South Africa. The ratio of ore to waste is about the same as in the pipe mines.

At the Mallin mine in the Transvaal a nearly vertical dike 2½ feet wide and 8,000 feet long is being mined underground by open stoping. The ore is crushed, jigged, and passed over grease tables. The workings have reached a depth of 600 feet. The ratio of ore to waste is not known, but is probably the same as in the pipe mines.

Mining and milling methods at the Williamson mine in Tanganyika and the DeBeers mines in South-West Africa are similar to the operations at the Bakawanga mine (*31*).

At the diamond placer mines in Angola, Congo (Leopoldville), Ghana, and Sierra Leone the overburden is removed by a combination of mechanical excavators and ground sluicing. The gravel is concentrated in diamond pans or jigs at movable washing plants. Concentrate then goes to central clean-up stations for final separation by grease tables, electrostatic separators, or by handpicking (*20*, *29*, *30*, *32*).

Virtually no data are available on the quantity of fine diamond remaining in the tailing from diamond concentrators because no practical method has been devised to measure the diamond content of materials. Thus far, when new concentrating methods have been developed, such as electrostatic separation and flotation, producers have had to determine the feasibility of recovering additional diamond from tailings by plant tests.

Sea mining of diamonds off the coast of South-West Africa started in 1961 in a pilot floating mining plant which was wrecked during a severe storm in June 1963. Its replacement was equipped in less than 3 months. Special anchors are put out in four directions to keep the vessel working under controlled conditions. Solids and salt water are brought up in 20 to 26 inch flexible tubes by compressed air and delivered to a scalping screen that removes coarse material. The water and fines are separated on a second vibrating screen and the diamondiferous fraction is sent to a heavy medium section. A hydrocyclone with a ferrosilicon slurry separates a heavy fraction containing diamonds. Diamond is finally recovered by handpicking.

Few of the South African diamond operations are mechanized. Usually the mining equipment consists of a pick, shovel, and batea.

In some instances crews using diving equipment work the bottoms of the rivers. The pay gravel is scraped from the bedrock, hoisted to surface, and panned to recover the diamond.

USES

The largest use for industrial diamond is in abrasive grinding wheels. Crushed bort and powder in the coarsest grit size commensurate with the finish desired are used.

Better quality rough and uncut and cut and polished stones from ¼ to 4 carats are set in holders and used to dress or true grinding wheels.

The smaller sizes of industrial stones (from 120 per carat to 3 per carat) or crushed bort are used in core, oil well, and blasthole drill bits (*7*).

Good quality cut and polished stones from ¼ to 4 carats are used for lathe tools and tools for thread and gear cutting. These stones are cleaved or shaped to adapt them for their intended use. For wire-drawing dies stones of the best quality in sizes from 20 per carat to 1 carat are required. First-quality stones for hardness indenters range in size from 12 per carat to 3 per carat. Whole diamonds and crushed bort and powder are used in diamond saws. Diamond powder is used to polish hard materials.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Gem-quality diamond is a coproduct of industrial diamond at most mines, accounting for over two-thirds of the value and about one-fifth of the quantity. At the Bakwanga mine, however, gems represent only about 2 percent of the quantity and 25 percent of the value of production. In South-West Africa over 90 percent of the quantity produced is of gem quality, representing at least 98 percent of the value. A few diamonds have been recovered from gold dredging in New South Wales.

ALTERNATE MATERIALS AND TECHNIQUES

Since 1945 various substitute processes for machining hard materials and sharpening carbide tools have been developed by industry. For some industrial applications they have been found to be as satisfactory as diamond grinding wheels or tools. These include electrodischarge processes, including electrosparking and electroarcing, electrolytic processes, ultrasonic abrasive grinding, silicon carbide belt grinding, and silicon carbide wheel grinding.

The technical applicability of these substitute methods is shown in table 1. In the drilling of small diameter deep holes, embossing, and tapping, the electrodischarge and the ultrasonic processes can be used where the diamond grinding wheel cannot be used.

TABLE 1.—*Technical applicability of substitute processes*

Machining and grinding operations	Electro-discharge	Electrolytic	Ultrasonic	Silicon carbide belts	Silicon carbide wheels
Cemented carbides	yes	yes	yes	yes	yes
Metals (steel, etc.)	yes	yes	yes	yes	yes
Nonmetals	no	no	yes	yes	yes
Large areas (greater than 4 square inches)	yes	yes	no	yes	(1)
Small areas	yes	yes	yes	yes	yes
Small diameter deep holes	yes	no	yes	no	no
Cut-off	yes	yes	yes	no	yes
Embossing	yes	no	yes	no	no
Off-hand grinding	(1)	yes	(1)	yes	yes
Fixed feed grinding	yes	yes	yes	yes	yes
Form grinding	yes	yes	yes	no	yes
Tapping	yes	no	yes	no	no

[1] Data not available.

The Bureau program on borides, carbides, nitrides, and silicides, described under Research, may develop substitutes for industrial diamond in some of its applications.

Boron nitride, synthesized by General Electric Co. and reported under the trade name, Borazon, is said to be as hard as diamond and to be capable of withstanding higher temperatures.

SYNTHETICS

The General Electric Co. announced the synthesis of diamond in 1955, after years of effort by many scientists in many countries. Virtually no data have been released on the raw materials or the process used, except that extremely high temperatures and pressures are employed. Since the announcement, General Electric Co. has been making an industrial diamond product competitive in quality and price with crushing bort from the Congo (Leopoldville). The company has not released production figures, but it is estimated that by 1963 output would be at the rate of about 4 to 5 million carats annually. Substantial quantities of manufactured diamond also were being made by Ultra-High Pressures Ltd. in plants at Springs near Johannesburg, Republic of South Africa, and at Shannon, Ireland. Other production occurred in Japan, Sweden, and U.S.S.R. Quantitative data are not available but it is probable that adequate facilities were being developed by U.S.S.R.

Industry tests of manufactured diamond in grinding wheels and other applications have shown the material is equal, and in some properties superior, to natural bort. Manufactured diamonds are nearly all single crystals, in contrast to the fragments and slivers of broken crystals that comprise much of the natural bort. Thus, the manufactured diamond has more sharp edges and points, which probably increases its abrasive efficiency (*3*, *16*).

The particle size distribution of the General Electric Co's ungraded manufactured diamond is given in table 2. Present research by General Electric Co. is directed toward improving shape of the crystals, and making larger crystals.

TABLE 2.—*Particle size distribution of ungraded manufactured diamond*

Mesh	Percent	Mesh	Percent
+40	0– 5	−170+230	15–22
−40+80	19–34	−230+325	6–10
−80+120	14–23	−325	5–15
−120+170	14–22		

SECONDARY SOURCES AND RECOVERY

The term "diamond salvage" is used to define the recovery of fine diamond fragments and powders that are present in the swarf and sludge from diamond grinding operations, as well as material from diamond-pointed tools, wheel dressers, diamond drill bits, and broken or discarded diamond wire-drawing dies and grinding wheels (*1*, *21*).

Since 1962 the salvage of diamond material from these sources in the United States has been about 2 million carats annually.

RESERVES

Reserves at the Bakwanga mine in the Congo (Leopoldville) have been blocked out by extensive shaft sinking and drilling. The reserve, estimated at 500 million carats in 1960, was believed to constitute 85 percent of the free world reserve of industrial diamond (*5*). Because of reworking of old ground, new information on old deposits, and the probable existence of considerable diamond off the coast of South-West Africa, the free world reserve of industrial diamond is estimated to be 600 million carats. Since the original estimates were conserative, the actual reserve may be much greater than now anticipated.

CONSERVATION PRACTICES

The development of heavy-medium and electrostatic separation methods permitted the

economic recovery of industrial diamond of much smaller particle size and enable the producing companies to rework old dumps. These methods have greatly expanded reserves of industrial diamond.

SOURCES OF STATISTICAL INFORMATION

The Bureau of the Census collects data on the imports, exports, and reexports of industrial diamond on a monthly basis. Data on diamond production are obtained from Department of State dispatches and mining company reports. Many of the data in the table listing the prodution of each field were compiled in collaboration with Dr. George Switzer, Chairman, Department of Mineral Sciences, Smithsonian Institution. The information through 1961 was compared with data published by Antoine Moyar of Brussels, Belgium, a recognized authority (*19*). No canvass is made of industrial diamond consumers.

PRODUCTION, CONSUMPTION, AND TRADE

Table 3 shows the world production of industrial diamond by countries. Imports during 1959–63 averaged 13,637,000 carats valued at $56,036,000; exports and reexports during the same period averaged 3,666,000 carats valued at $18,531,000. Data on consumption are not available.

There is no import duty on industrial diamond except synthetic diamond and diamond advanced in condition or value. There is a 15 percent ad valorum duty on each of these.

TABLE 3.—*Primary industrial diamond production*

(Thousand carats)

	1954–58 (average)	1959	1960	1961	1962	1963
Africa:						
Angola	331	500	400	460	319	325
Central African Republic	83	60	50	70	185	282
Congo (Leopoldville)	13,764	14,200	13,040	17,740	14,400	14,468
Congo (Brazzaville)[1]					2,471	5,343
Ghana	1,741	2,200	2,500	2,560	2,580	2,142
Guinea	184	400	670	730	210	32
Ivory Coast			120	330	182	117
Liberia (exports)[2]					680	508
Sierra Leone	796	1,150	1,450	1,997	1,200	833
South Africa, Republic of:						
"Pipe" mines:						
Premier	1,072	950	1,000	1,200	1,260	1,565
DeBeers Group	458	500	580	760	750	754
Others	84	70	100	80	84	86
"Alluvial" mines	73	150	160	160	190	196
South-West Africa	88	90	50	90	227	119
Tanganyika	195	350	250	345	324	313
Total	18,869	20,620	20,370	26,522	25,061	27,082
Other areas:						
Brazil[3]	130	170	175	175	175	175
British Guiana	18	40	40	45	40	40
Venezuela	85	80	57	73	83	31
Australia, Borneo, India, and U.S.S.R.	4	10	360	420	[4] 2,300	[4] 2,760
World total	19,106	20,900	21,000	27,200	27,659	30,088

[1] Probable origin, Congo (Leopoldville).
[2] Exports reported under production from Sierra Leone prior to 1962.
[3] Estimate.
[4] Estimate, production from U.S.S.R. only.

STRATEGIC CONSIDERATIONS

Industrial stones and bort have been designated as strategic and critical materials for stockpiling. At the end of 1963 the United States had the capacity to produce 4 to 5 million carats of manufactured diamond and 2 million carats of salvaged material, annually, more than one-half of its requirements of crushed or under 40-mesh size industrial diamond. The United States will continue to be dependent on foreign sources, principally Africa, for all of its requirements of material larger than 40-mesh until such time as larger size diamonds can be or are synthetically produced. Stockpile commitments for industrial stones have been met and comprise an emergency supply. On June 30, 1964, Government inventories of industrial stones totaled 24.7 million carats, of which 9.3 million was in the national (strategic) stockpile and 15.4 million in the supplemental stockpile. Stocks of crush-

ing bort totaled 36.6 million, of which 31.1 million was in the national (strategic) stockpile and 5.5 million in the supplemental stockpile.

Although 98 percent of the natural diamond requirements of the free world come from Africa, the total weight of the annual production is only between 4 and 5 tons, so the entire quantity could be dispatched to the United States by air, provided the African supply remains available.

The industrial diamond product manufacturing is distributed through the Northeast States, with its principal concentration in the New York, N.Y., and Newark, N.J., area. There are a few firms in the Midwest and in the Los Angeles, Calif., area.

PRICES

Crushing bort comprises the largest fraction of industrial diamond, sales, and its price is indicative of the price trends of other types. Prices of crushing bort in New York are the London quotations shown in table 4 plus transportation, insurance (all types), and broker commissions.

TABLE 4.—*Average value of industrial diamond imported for consumption into the United States, and the published price of crushing bort in London, per carat*

Year	Value of imports, industrial diamond	London price of crushing bort
1954–58 (average)	$4.11	$2.44
1959	4.78	2.80
1960	3.94	2.80
1961	4.82	2.80
1962	4.16	2.80
1963	4.20	2.80

On June 2, 1958, the General Electric Co. reduced its prices on ungraded manufactured diamond 15 percent to 24 percent, depending on quantity, from the prices quoted on January 1, 1958, as given in table 5; prices for graded diamond in effect December 31, 1963, are also given. Prices of ungraded fines and micron sizes were available on application.

TABLE 5.—*Prices per carat of manufactured diamond*

Quantity (carats)	Jan. 1, 1958	June 2, 1958	Dec. 1963
500	$4.14	$3.15	$2.85
1,000	3.91	3.10	2.85
2,500		3.05	2.80
10,000	3.48	2.96	2.74

RESEARCH

Continued research on diamond synthesis is being conducted by General Electric Co. in the United States and by others abroad to increase the size of the diamond, control the crystal size distribution, improve control of crystal shape, and to lower manufacturing costs.

Industrial Distributors maintains the Diamond Research Laboratory at Johannesburg, Republic of South Africa, devoted to basic and applied research on industrial diamond. The aims of the research center are to promote and extend the industrial uses of diamond, and to improve and promote methods of its recovery and conservation. The services of the laboratory are available to any user or producer of diamond. This is the only laboratory in the world devoted solely to diamond research. A branch of this laboratory was established in Canada in 1959.

Since 1946, the Bureau of Mines has conducted continuing research on techniques for production, fabrication, and testing of numerous metallic borides, carbides, nitrides, and silicides. Some of these compounds may develop into suitable diamond substitutes.

Research is being conducted by industry to improve performance of diamond grinding wheels, through the use of superior bonds, new methods for inserting grains, new operating techniques, and the more extensive and intelligent application of coolants (*6, 25, 26*).

Improvements in diamond drills and in drilling techniques brought about by research have contributed to growth in this phase of the diamond industry (*14, 15, 23*).

OUTLOOK

The importance of sources of industrial diamond will likely be unchanged in the near future. Africa will remain the greatest source of natural industrial diamond. Manufactured diamond will constitute the second largest source, and the quantity of recovered diamond bort will increase.

Continued research, in the United States and abroad, will result in further improvements in the manufacture of diamond which should permit lower costs and even better quality control of the finished product. The upper limits of particle size of manufactured grit has increased and is expected to increase above the 20-mesh size that can now be made. The probability of manufacturing larger material cannot be fully appraised, but significant progress is being made.

Research on borides, carbides, nitrides, and silicides may result in developing compounds

competitive with diamond in some applications. Some properties of synthetic compounds may be superior to those of diamond.

Domestic consumption of industrial diamond has been the fastest growing segment of the abrasive industry and has increased at a rate greatly exceeding gross national product in constant dollars. With an improved supply and price outlook, the continuing trend toward increased automation in grinding operations, superior abrasive properties of diamond, expanded use of diamond abrasives for old applications and the development of new uses is expected to contribute to the increase in U.S. consumption of diamond for the next several years. Continued developments in the control of size and shape of manufactured diamond may result in the increased use of this material but not a replacement of substitute methods for grinding cemented carbides and other hard materials developed when industrial diamond was in tight supply. Industry will continue to increase the efficiency of grinding wheels and diamond tools through research.

PROBLEMS

The diamond industry shares the major problems of the abrasive industry, which include a lack of low-cost effective substitutes for industrial diamond, lack of knowledge on forming large diamond crystals, and a lack of definitive methods of evaluating the comparative abrasive properties of the various minerals and materials. Hardness, per se, does not assure that a material will be a good abrasive (*12*). Other factors, including type of fracture, crystal form, friability, and ability to withstand temperature changes also determine abrasive value.

A continuing problem confronting diamond producers is how to evaluate the efficiency of diamond recovery processes because of a lack of practical methods to measure diamond content of ores and residues.

Other problems are the lack of domestic deposits of natural diamond and the lack of data on the consumption of industrial diamond by grades and uses, which would be of invaluable assistance to industry and in mobilization planning.

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DIATOMITE

By Benjamin Petkof [1]

MICROSCOPIC water plants called diatoms secreted silica from the prehistoric seas in which they lived. Upon their death their silicified remains settled to the bottom and formed sedimentary deposits of amorphous silica of great depth. This material, referred to as diatomite, possesses certain physical properties which make it valuable as a filter medium, as industrial filler, for thermal and accoustical insulation, and for many other purposes.

The United States leads the world in production, with primary production in California. Production during 1960–62 averaged more than 482,000 short tons per year, valued at about $24 million.

The principal problems confronting the industry concern the search for new uses, development of specialized processes and equipment for improvement of efficiency and product quality, health hazards, high transportation cost, and need for markets for low-quality diatomite and any coproducts developed during mining.

BACKGROUND

In A.D. 532, the Roman Emperor Justinian I used diatomite brick to lighten construction of a dome 107 feet in diameter in the church of St. Sophia in Constantinople. The first large-scale application of diatomite was as an absorbent for liquid nitroglycerine, developed by Alfred Nobel in 1886; this use is now obsolete. The first extensive use to survive was for filtration of raw cane sugar liquor. This application dates from 1876, when diatomite began to replace paper pulp, compressed cotton, and asbestos-cellulose filter pads (*2*, *6*).[2]

The most important developed domestic deposits were discovered about 1890 near Lompoc, Calif. Insulating brick cut from naturally consolidated diatomite was the first quantity product of the Lompoc mines. In 1906, the first mill was built at Lompoc to pulverize the diatomite. In 1912, new owners of the Lompoc quarries organized the Kieselguhr Co. of America and began a program to develop diatomite as a filter aid. Subsequently, the firm name was changed to Celite Co. This organization acquired extensive adjoining acreage in 1926, and 2 years later was sold to the Johns-Manville Corp. Great Lakes Carbon Corp. has since acquired and developed a large acreage in the Lompoc area (*11*).

SIZE AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

The United States is the largest world producer and user of diatomite. During 1963, 15 plants operated by 13 companies produced diatomite. In 1962, 12 companies operated 14 plants, producing an average of 482,000 short tons per year valued at about $24 million. California produced the bulk of domestic supply with smaller quantities from Nevada and Washington. Arizona, Maryland, and Oregon provided minor quantities.

The major producers during 1963 were Johns-Manville Corp. at Lompoc, Calif.; Great Lakes Carbon Corp., at Lompoc, Calif., and Basalt, Nev.; The Eagle-Picher Co. at Colado and Clarke Station, Nev.; and the Airox Co. at Santa Maria, Calif. The remaining nine producers, in Arizona, California, Maryland, Nevada, Oregon, and Washington, furnished about 7 percent of the total production.

Diatomite is mined in the U.S.S.R., Denmark, France, West Germany, Italy, the United Kingdom, and other countries.

[1] Commodity specialist.
[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS *(4, 8—10)*

The terms "diatomite", "diatomaceous earth", and "kieselguhr" are synonymous and currently preferred for this commodity. Erroneous nomenclature occasionally encountered includes infusorial earth, infusorial silica, tripolite, and other local designations.

Diatomite is largely a fossil accumulation of diatoms, usually with some radiolaria and smaller amounts of foraminifera. These are all microfossils, diatoms being planktonic siliceous plant organisms, while radiolaria are planktonic siliceous, single-cell animal organisms. Foraminifera are calcareous animal organisms. Diatomite is essentially amorphous, hydrated, or opaline silica with various contaminants, such as silica sand, clay minerals, iron, alkalies, and alkaline earths. The chemically combined water ranges from 3½ to 8½ percent. Apparent density of dry consolidated material varies from 20 to 40 pounds per cubic foot, and the dry powder from 5 to 16 pounds per cubic foot.

Unprocessed diatomite has a hardness between 4 and 6½ on Mohs' scale. It is softer than opal, and appears to be only slightly harder than brass, which is considered 3½ on Mohs' scale.

Qualities responsible for the wide use of diatomite include its structure, porosity, low apparent density, strength, elasticity, chemical inertness, low thermal conductivity, light color, high melting point, and large surface area per unit of weight.

Three general grades of prepared diatomite are based on heat treatment after the usual drying and reduction stages. These grades are called "natural," "calcined" or "pink," and "flux calcined" or "white." The natural is that material sold without heat treatment after drying, delumping, and air classification. The calcined grade is similarly processed and is heat-treated in direct-fired rotary kilns using gas or fuel oil without fluxes, while flux-calcined material is calcined with the addition of a fusible alkali salt.

The Great Lakes Carbon Corp. markets its processed diatomite under the trade name of Dicalite, Eagle-Picher Co. Celatom, and Johns-Manville as Celite. The various processed grades are also named or numbered by each company for designating material with certain standardized qualities, such as color, brightness, particle size range and distribution, chemical analyses, and filtering speed.

TABLE 1.—*Typical chemical analyses of processed diatomite (dry basis)*

	Natural (percent)	Calcined (percent)	White (percent)
SiO_2	86.8	91.0	87.9
Al_2O_3	4.1	4.6	5.9
Fe_2O_3	1.6	1.9	1.1
CaO	1.7	1.4	1.1
MgO	.4	.4	.3
Ignition loss	4.6	.3	.1
Undetermined	.8	.4	3.6

TECHNOLOGY

Geology *(2, 4, 6, 11)*

The principal commercially developed diatomite deposits were formed in the late Miocene to early Pliocene ages when volcanic activity furnished silica-rich waters combined with ideal sunlight conditions and plant food supply. Each diatom extracted silica from the waters, secreting it to form minute, siliceous, two-halved envelopes or frustules with various intricate and often symmetrical designs. The two halves are not hinged but fit together. A small diatom measures less than 10 microns, a large diatom 100 microns or more.

The fossil species involved are single-celled algae. More than 12,000 different frustule patterns have been identified. These are microporous structures, many containing substructures only visible under the electron microscope. Although fossil frustules are known to be more than 25 million years old, these shells are identical to those of their living descendants.

Some diatomite beds are of fresh water origin, while others accumulated in ocean waters. Both lake and marine varieties are mined commercially; the frustule patterns of the diatoms from the two sources differ considerably so that the sources of each can be determined with a microscope.

The porous structure of individual diatoms and their massed arrangement impart unusual filtering properties to diatomite. When used as a coating on filter cloth diatomite strains out microbes and colloids from liquids and still permits relatively rapid flow of the filtrate. The filter coating is about 90 percent voids.

Some authorities believe that the marine diatoms of the Pacific Coast propagated in the colder climates of the north Pacific during the Miocene and were carried south by ocean currents and trapped in protected coves of the California coast.

As zones of varying hardness are found in many deposits, particularly near the surface, sampling must be conducted to depth.

Mining (2, 5–6, 9, 11)

All current mining is by open pit. The first step is to remove the overburden with high-speed, power-driven scraper-carriers or bulldozers. Thickness of overburden ranges from 1 to 15 times the thickness of recoverable and usable diatomite. After exposing the diatomite, the mining is done either with the same carryalls used for stripping overburden or with power shovels, loading into trucks. The Johns-Manville Corp. hauls the crude to a series of glory-hole storage shafts at strategic points in the deposit and above a tunnel system. These tunnels terminate near central storage bins close to the mill where crudes of differing grades can be segregated for specification blending.

Mining is complicated by faulting, combined with interbedding of contaminated material which must be wasted. In the Lompoc, Calif., area, selective mining is done within a total vertical thickness of about 1,000 feet. The purest material lies in a series of beds stratified with thin layers of volcanic ash down to the 500-foot level. Stratification lines are seldom more than one-fourth inch thick. Below this zone is a conchoidally fracturing bed several hundred feet thick contaminated with argillaceous material up to 10 percent alumina. Under these two beds may be another series of varying purity, also interstratified with argillaceous diatomite and volcanic ash.

In some cases wet ore goes to a storage area at the quarry where air drying takes place. It is loaded into bottom-dump trailer trucks by bulldozer or slusher hoist and slackline cable drag-scraper for transporting to the mill.

Milling (2, 5–6, 9, 11)

The cost of a plant to process 50,000 tons of diatomite per year is about $2.8 million. Because of the climate, Western plants are of the outdoor type and house only the packing and storage departments and operating control room.

The process outlined diagrammatically in figure 1 covers the Great Lakes Carbon Corp. plant at Lompoc, Calif., which is typical of large-scale diatomite processing.

Diatomite freshly mined from the Lompoc area frequently carries 50-percent moisture by weight; in which case 1 ton of water must be evaporated for each ton of dry diatomite produced—an expensive step in the processing. Drying is accomplished in a hot pneumatic system embodying flash-drying, combination blower-hammer mill comminution, air cyclones, and dust collectors. The diatomite is transported through the system by moving hot gases.

The processing system has three general divisions—a wet-end circut, a calcining section, and a finishing circuit. Crude ore passes through a crusher to a storage bin, discharging to a combination miller-blower with simultaneous injection of a large volume of hot air from a direct-fired oil or gas furnace. The blower injects the ore and hot gases into a system of cyclones and dust collectors, which release air and moisture to the atmosphere, sludge waste to a settling pond, and dry diatomite to the calcining kiln. Impurities not eliminated in the wet-end circuit are usually removed in the finish-end separators.

When flux calcining takes place, 3 to 10 percent by weight of either soda ash, sodium chloride, or caustic soda is added at the crude ore storage bin. Calcination affects the filtering properties of diatomite by changing the surface texture, agglomerating fines, and converting clay minerals which were not removed in the wet-end circuit to aluminum silicate slag. These slag particles are then largely eliminated in the finish-end trapping circuit. Organic matter is removed by combustion during calcination.

Calcination with fusible alkali salts reduces the diatomite surface area per unit volume of the finished product. It also whitens the product, thus increasing its value as a filler where color is significant. Kiln feed temperature is 300° to 400° F; maximum discharge temperature is 2,200° F.

The calcine drops to a hammer mill in which lumps are broken and passes to a milling blower, further reducing the particle size and carrying the calcine to air separators. Any dense particles still in the circuit are trapped in one of these separators and eliminated as a final waste product discharge.

The last air classifier exhausts a fine finished product to a baghouse while discharging a coarser main product. Both of these finished products go to storage hoppers and bagging machines where they are packed in 50-pound paper or cloth bags.

Waste products comprise about 16 percent of total feed.

USES (2, 4–6, 8–10, 12)

The primary industrial application of diatomite is as an industrial filtration medium for liquids ranging from municipal water supplies to alcoholic beverages. Additional uses for diaomite are as fillers, as thermal and accoustic insulation, and for miscellaneous uses such as absorbents, abrasives, polishes, catalyst carriers, glazes, paints, pozzolan, anticaking agent, insecticides, fungicides, fabrication of synthetic silicates, and lightweight aggregate.

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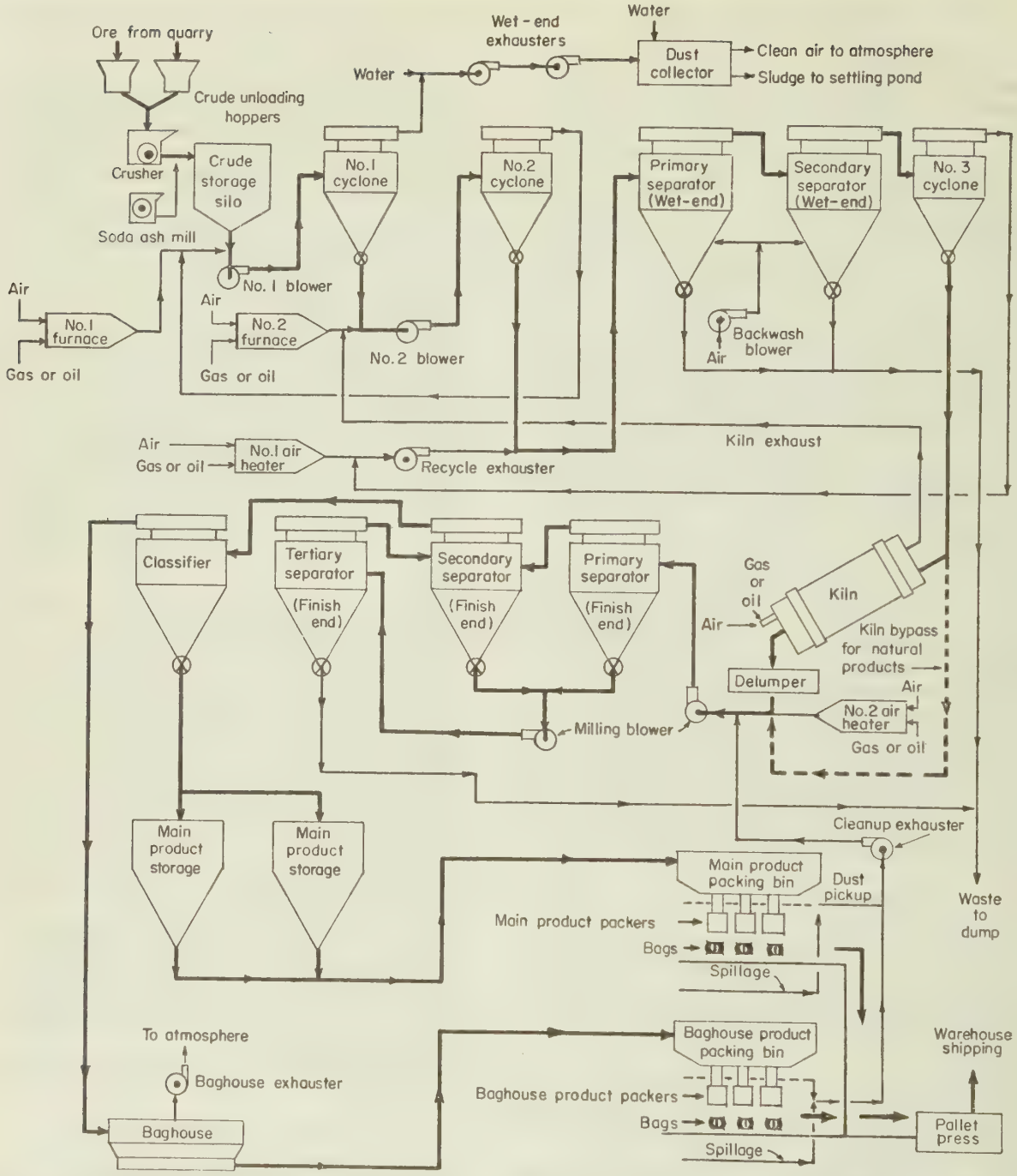

FIGURE 1.—Flowsheet for the Processing of Diatomaceous Earth at Great Lakes Carbon Corp., Lompoc, Calif.

Products filtered with the aid of diatomite include sugar liquor, alcoholic and nonalcoholic beverages, acids, water, petroleum compounds, varnishes, shellac, waxes, greases, resins, plating and dry-cleaning solutions, vegetable oils, gelatins, and antibiotics.

Industrial filters have frameworks supporting filter cloths or wire mesh on which a precoat or cake of porous filter-aid material, usually diatomite, is uniformly deposited. By a difference in pressure between the two sides of this septum, the liquid from the liquid-solids mixture is forced through the filter aid and filter cloth so that the solids to be filtered out are deposited on the precoat.

The continuous filter cycle is started by filling the circuit with a mixture of clear liquid and filter aid until a precoat 1 to 2 inches thick is deposited on the filter cloth. The pulp to be filtered is then introduced with periodic additions of filter aid so that a porous sludge is being constantly deposited on the precoat.

As a mineral filler or extender diatomite is low in cost and imparts such desirable physical properties as light unit weight, strength, elasticity, chemical inertness, low heat conductivity, light color, and reduces reflection of light (flatting agent). Its market as a filler is largely in paint, asphalt, rubber, paper, plastics, and insecticides.

As diatomite is composed of about 90 percent voids and has a relatively high melting point it is a good insulator against heat and sound. It consequently finds applications in furnaces, kilns, refrigerators, safes, and building construction as either brick, shapes, or loose fill.

ALTERNATE MATERIALS

Expanded perlite and silica sand can replace diatomite as a filtration medium. Talc, ground silica sand, barite, gypsum, wollastonite, clay, perlite, vermiculite, chalk, and ground limestone are filler substitutes for diatomite.

Vermiculite, perlite, cinders, expanded clay, shale, and slag can replace diatomite as material usable for lightweight aggregate. When used for insulation, diatomite competes with high-alumina brick, fire clay, asbestos, kyanite, synthetic mullite, mineral wool, expanded vermiculite, and perlite.

RESERVES

Domestic deposits are widely distributed throughout the country. The best known deposits and reserves occur in the West and the largest known reserve, currently being mined, lies near Lompoc, Calif. This deposit extends over many hundreds of acres with beds reaching 1,400 feet in thickness. Arizona, Nevada, Oregon, and Washington currently produce diatomite and have large undetermined reserves of material. The Western States are capable of meeting national requirements for many years. Deposits also occur in nearly all Atlantic coast States from Maine to Florida. However, these deposits have been unable to compete with western material (*4*).

Adequate published information on foreign reserves is not available, but diatomite deposits occur on every continent. Deposits capable of sustaining a processing plant have been confirmed in Iceland. A proved reserve of approximately 6 million tons is available in Kenya, Africa, with an additional 4 million tons estimated to be available. Additional deposits are known in numerous countries with undetermined reserves (*12*).

PRODUCTION, CONSUMPTION, AND TRADE (*12*)

Bureau of Mines statistics are collected on the basis of sales and use of mined diatomite by both producers and consumers. Therefore, the data shown in table 2 are representative of both production and of consumption plus exports.

Government records of imports or exports of diatomite are not available. Presumably very little material is imported because of high transportation costs from most foreign countries. U.S. producers export better quality prepared diatomite, but the quantity is believed to be small.

Crude or processed diatomite may be imported duty free.

World production of diatomite is shown by countries in table 3.

TABLE 2.—*Diatomite sold or used by producers in the United States, 3-year totals*

Years	Quantity, short tons	Average value per ton
1945–47	640, 764	$20. 17
1948–50	722, 670	25. 55
1951–53	908, 448	29. 97
1954–56	1, 105, 279	39. 21
1957–59	1, 349, 340	45. 73
1960–62	1, 446, 625	50. 08

PRICES AND COSTS

Prices vary according to purity of the diatomite, its particle size range, whether it is uncalcined, calcined, or flux calcined, whether it is in bulk or bagged, and the type of bag used.

Average prices of diatomite during 1963 are presented in table 4. These values were obtained from direct canvass of the industry by the Bureau of Mines.

TABLE 3.—*World production of diatomite, by countries* [1] [2]

[Short tons]

Country [1]	1954–58 (average)	1959	1960	1961	1962	1963
North America:						
Canada	34	5	44	214	211	322
Costa Rica	2, 860	2, 425	2, 425	717	827	[3] 2,000
Guatemala	17, 576					
Nicaragua		1, 887	2, 249	2, 976	1, 414	[3] 1, 400
United States	400, 968	[4] 449, 789	[5] 482, 202	[5] 482, 202	[5] 482, 202	[5] 482, 202
South America:						
Argentina	4, 233	4, 829	117	1, 286	180	[3] 1, 000
Chile	117.					
Colombia	187	330	440	330	150	[3] 150
Peru	39	254	1, 284	2, 048	1, 624	[3] 1, 600
Europe:						
Austria	4, 275	4, 492	4, 431	5, 993	4, 613	[3] 4, 500
Denmark:						
Diatomite	15, 895	18, 200	17, 600	21, 500	22, 000	[3] 22, 000
Moler [3] [6]	193, 500	205, 000	204, 300	212, 900	230, 800	220, 500
Finland	2, 030	1, 520	1, 457	805	1, 323	[3] 1, 300
France [7]	81, 216	112, 821	140, 468	118, 429	[3] 110, 000	[3] 110, 000
Germany, West [7] (marketable)	64, 796	55, 737	51, 138	72, 201	67, 792	[3] 66, 000
Italy	22, 196	57, 099	51, 888	[3] 55, 000	[3] 55, 000	[3] 55, 000
Portugal [7]	1, 853	2, 075	1, 172	847	1, 598	[3] 1, 600
Spain [7]	13, 138	11, 561	13, 840	19, 351	13, 352	[3] 13, 000
Sweden	1, 292	764	453	783	[3] 770	[3] 770
U.S.S.R. [3]	[8]	275, 000	300, 000	330, 000	330, 000	345, 000
United Kingdom	25, 409	[3] 19, 000	16, 553	24, 920	[3] 24, 900	[3] 24, 900
Yugoslavia	[3] 4, 400	[3] 5, 000	[3] 5, 000	[3] 5, 000	4, 500	[3] 4, 500
Asia: Korea, Republic of	2, 134	1, 865	2, 646	1, 989	758	2, 407
Africa:						
Algeria	29, 280	38, 087	24, 266	34, 315	30, 534	[3] 9, 000
Kenya	4, 200	4, 041	3, 791	3, 537	3, 207	[3] 3, 300
Mozambique	22		103	397		
Southern Rhodesia [7]		148	164	409	423	301
South Africa, Republic of	700	397	346	137	647	[3] 250
United Arab Republic (Egypt)	364	440	805	332	55	[3] 55
Oceania:						
Australia	5, 988	5, 700	5, 218	6, 067	8, 189	[3] 4, 700
New Zealand	2, 167	8, 152	6, 992	3, 961	2, 099	[3] 2, 200
World total (estimate) [1] [2]	1, 235, 000	1, 480, 000	1, 550, 000	1, 635, 000	1, 630, 000	1, 610, 000

[1] Diatomaceous earth is produced in Brazil, Bulgaria, and Japan, but data on output are not available; estimates are included in total. Hungary and Rumania may produce diatomaceous earth, but data are not available and no estimates are included in total.

[2] This table incorporates some revisions. Data do not add exactly to totals shown because of rounding where estimated figures are included in the detail.

[3] Estimate.

[4] Average annual production 1957–59.

[5] Average annual production 1960–62.

[6] A clay-contaminated diatomite used principally for lightweight building brick.

[7] Includes Tripoli.

[8] Data not available; estimate included in total.

TABLE 4.—*Average value per ton of diatomite in 1963*

Use	Value
Filtration	$62. 26
Insulation	49. 91
Abrasive	137. 00
Fillers	50. 07
Miscellaneous	30. 20

TAXES

Producers are accorded a 15-percent depletion allowance in computing Federal income tax on diatomite operations.

TRANSPORTATION

Transportation of diatomite is an important economic factor in the industry. This low-density, high-bulk material must be moved from western production areas in California and

Nevada to the highly industrialized East and Middle West where it is used.

RESEARCH

Several large producers maintain laboratory facilities and engage in research into new uses, improvements, and product standardization. Additional research is carried at the university level, especially in the area of filtration and filter aids. Recent Bureau work has been limited to the investigation of the diatomite-bearing strata of Choctaw and Clark Counties, Ala. (7).

OUTLOOK

Recent data indicate that diatomite production for various industrial uses has been steadily increasing at an average annual rate of about 5 percent. The demand for diatomite should continue, and a small but steady production increase can be expected.

Individual uses such as filtration, filter aid, industrial filters, insulation, and other miscellaneous uses have shown a steady or increasing demand since 1959. The abrasive use of diatomite is small and has steadily decreased; in time it may cease completely.

The increasing demand for diatomite may encourage exploration for new deposits and eventual exploitation of less desirable impure deposits.

Applied research by diatomite users and producers will continue to develop new applications for this nonmetallic mineral. Additional research and resource investigations may be carried out by the Bureau of Mines and the various agencies of diatomite-producing States.

Domestic reserves of diatomite are adequate for the forseeable future.

PROBLEMS

Shortage of high-grade diatomite deposits in the eastern and central sections of the country and lack of economical techniques to beneficiate low-grade diatomite are obstacles to the development of diatomite production closer to major consuming markets.

The high cost of transporting diatomite from the current major producing areas in the Western States to the principal markets in the highly industrialized Eastern and Central States remains a primary industry problem.

Potential newcomers in the industry are handicapped by the limited availability of information on methods of testing, beneficiation, and other technical data. Almost all research is sponsored by industry, and results are not published.

Processing problems occur in the industry which require the development of special techniques. The high ratio of water in some newly mined diatomites, the fragile character of the material, and the complex specifications required for the final product are examples of industry problems.

If rigid precautions are not observed, diatomite dust can cause pneumoconiosis among workers, especially in plant areas where dust from calcining operations is present (*1*, *3*).

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FELDSPAR

By J. Robert Wells [1]

FELDSPAR production in the United States has grown with general industrial expansion since the commencement of the pottery industry in the 1850's. An alltime production high of 560,000 long tons of crude feldspar was reached in 1956.

Ten companies produce more than 90 percent of crude feldspar mined and market most of the feldspar sold in the United States. There are many small producers of crude feldspar, most of which sell to the larger producers and grinders. Feldspar deposits are widely scattered throughout the United States, but production is centered in the Southeast, New England, the Rocky Mountains, and California.

Feldspars are anhydrous aluminum silicates of potassium, sodium, or calcium in which one base generally predominates. Feldspar is ground to various mesh sizes and sold to the ceramic industry as a flux and as a source of alumina.

Feldspar and feldspathic rocks and sands are mined by various methods depending on the type of deposit. Pegmatite deposits with large crystals of feldspar are mined by small- and large-scale methods followed by hand cobbing and hand sorting, and by mass mining methods with subsequent flotation or electrostatic concentration. Feldspathic rocks are mined by large-scale methods and concentrated by flotation. Feldspathic sand deposits are mined by dragline excavators. Feldspar-silica mixtures are also produced as byproducts of granite quarrying by beneficiation of discarded fines.

Ore for flotation feed is crushed and wet-ground in rodmills to minus 20-mesh. Feldspar from sands is concentrated by flotation, but in some cases feldspar-sand mixtures are used directly in glass manufacture. Iron and iron-bearing minerals are removed from feldspar by magnetic separators; quartz and feldspar may be separated electrostatically, but the practicality of the process has not been proved. Most finely ground feldspar is dry ground in silex-lined pebble mills. The principal byproducts of feldspar mining are quartz and mica.

Feldspar is used principally as a flux in making glass, pottery, porcelain, enamel, tile, and other ceramic products.

Nepheline syenite and aplite are the major substitutes for feldspar as sources of alkalies and alumina. Other substitutes, depending on use, are talc and pyrophyllite.

Although nepheline syenite and some feldspar are imported from Canada, the United States is self-sufficient in feldspar. World reserves are adequate.

The outlook for the feldspar industry is for a gradual growth paralleling the gross national product with substitutes continuing to supply a significant part of the demand. Feldspar recovered by froth flotation has reached nearly 70 percent of the total domestic production.

The major problems of the industry are high production costs for hand-cobbed material, inadequate data on massive high-grade deposits, transportation costs, and competition from substitutes.

BACKGROUND

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Feldspar was first mined in the United States in North Carolina in 1744 and shipped to England. Earliest recorded production for local consumption was from a deposit in Connecticut in 1825, and the first feldspar mill was set up at the Toll Gate mine, south of Middletown, Conn., about 1850. Since then, the feldspar mining industry has expanded with the industrial growth of the country, and production of

[1] Commodity specialist.

crude feldspar reached the alltime high of 560,000 long tons in 1956. Since 1956 production has averaged 510,000 long tons per year.

The three leading feldspar companies supply 65 percent and the next seven firms supply 27 percent of marketable feldspar production in the United States. A large number of firms and individuals supply the remaining 8 percent. There has been a gradual consolidation and absorption of the smaller firms into the larger ones. Most of the small producers operate intermittently and sell their crude ore to larger producing companies or independent mills. A small quantity of crude ore is sold directly to consumers who grind it to their own specifications.

In 1940, a large-scale pilot plant operation of a froth flotation process developed by the Bureau of Mines indicated that greatly reduced production costs could be achieved for glass feldspar. This resulted in the first commercial flotation plant at Kona, N.C., in 1946. Ten froth flotation plants are now operated by seven of the large companies to recover feldspar concentrate from pegmatite and alaskite. Feldspar is recovered from California dune sands by two companies, one of which uses froth flotation. In 1963 about 66 percent of the marketable feldspar produced was recovered by froth flotation.

Feldspar concentrate is sold mostly to glass and pottery manufacturers, with about 5 percent going to other industries. Some of the companies employing flotation also produce feldspar from hand-cobbed or sorted ore (crushed and sorted on conveyor belts). Some companies produce only hand-cobbed or sorted ore. The smaller operators produce only hand-cobbed material.

Feldspar is mined in at least 35 countries. Owing to its wide distribution and low unit cost, feldspar trade between countries is not great. Leading free world producers in order of production are the United States, West Germany, Italy, France, Sweden, Norway, Japan, and the Republic of South Africa. U.S. mine production has been reported from more than half of the States, but production in 1959–63 was centered in North Carolina, California, Connecticut, Georgia, South Carolina, South Dakota, New Hampshire, Virginia, Arizona, and Maine, in order of production. Most grinding mills are in feldspar mining areas, and some are in the immediate vicinity of the larger mines. Some merchant grinders are in consuming areas.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Feldspar is a term applied to a group of igneous minerals consisting chiefly of aluminosilicates of potassium, sodium, and calcium; one base usually predominates.

Orthoclase and microcline, the most common potash feldspars, have the same composition, $KAlSi_3O_8$, and differ only in crystalline form. Anorthoclase is a feldspar in which part of the potash is replaced by soda. A small quantity of anorthite may be present. The soda-lime feldspars, called the plagioclase group, form an isomorphous series with albite or "soda spar" ($NaAlSi_3O_8$) at one extreme and anorthite or "lime spar" ($CaAl_2Si_2O_8$) at the other. Anorthosite is a mixture of albite and anorthite.

Cornwall stone, imported from England, is a highly weathered and partly kaolinized feldspathic rock used to replace feldspar and kaolin in some ceramic applications.

Lithospar is a term used by the feldspar industry to designate a naturally occurring mixture of spodumene and feldspar.

Potash and soda feldspars both are used, but potash feldspars are preferred for most ceramic uses. Grades of feldspar are identified by their end use. Glass grade must be 99.5 percent through 20-mesh and must not contain over 0.05 percent iron oxide; amber glass grade may contain up to 0.50 percent iron oxide. Ceramic grades range from 120- to 325-mesh.

Some companies designate their products by number; the grade with the highest potash content is No. 1 and No. 2 is a lower grade. There may be two or more mesh sizes for one number; for example, No. 1, 230-mesh, and No. 1, 200-mesh. Some feldspars are designated by alkali content (the sum of K_2O and Na_2O present), and some by the alkali ratio (the ratio of K_2O to Na_2O in the ore). For some uses the free quartz content of the final product must be designated.

There are no rigid specifications for feldspar. Commercial Standard CS 23–30 by the National Bureau of Standards has received little acceptance (*10*).[2]

TECHNOLOGY

Geology

Feldspar may be white, grayish yellow, yellow, shades of red from light rose to brick, green, or bluish depending on impurities. It has a vitreous to pearly luster, an uneven fracture, and a hardness of 6.0 to 6.5 according to

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

Mohs' scale. The specific gravity is 2.54 to 2.76, the refractive index is 1.524 to 1.584, and the melting point is 1,100° to 1,522° C.

The feldspars are mong the most widely distributed of rock-forming minerals, and they occur as constituents of most rocks. Feldspar occurs in crystals large enough for selective mining only in dikes formed where the crystallization from molten magma has been slow.

Feldspar-bearing pegmatite dikes can range in width from stringers to masses over 100 feet across, and single crystals can be from several inches to several feet long. Occasionally, crystallization is exceptionally coarse or the constituents of the dike are separated into distinct zones. In such cases feldspar can be obtained in commercial quantities virtually free from associated minerals by simple hand sorting.

Quartz and muscovite mica are always associated with feldspar in dike deposits. Common accessory minerals include tourmaline, pyrite, biotite, hornblende, garnet, and magnetite, all iron-bearing minerals. Pegmatite may also contain such minerals as spodumene, beryl, columbite, tantalite, and cassiterite.

Granite sometimes contains as much as 60 percent feldspar as fairly coarse crystals. These crystals, however, often contain disseminated iron-bearing minerals which render the feldspar worthless for most commercial uses.

Alaskite is an igneous rock consisting essentially of quartz, mica, and feldspar intermingled in an irregular texture. The feldspar grain size is larger than that in the average granite, but alaskite seldom can be treated by hand picking. Three companies mine alaskite from a large deposit in North Carolina and beneficiate it by flotation to recover all three major constituents. The feldspar product is a mixture of potash and soda feldspar, the K_2O content ranging from 4 to 8 percent.

Commercially minable quantities of feldspar occur in some beach and river sands.

Mining

Feldspar deposits are mined chiefly by open-pit methods, although a few mines are underground.

Feldspar-bearing dikes are usually steeply inclined bodies with well-defined boundaries which can be worked with little or no removal of wall rock in the early stage of mining.

In zoned pegmatites, only the feldspar portions of the deposit are mined. Development usually proceeds from surface pits or from side-hill cuts, depending on the nature of the outcrop. Sometimes dikes with a long surface strike are mined by a series of pits opened simultaneously or successively on zones of clean feldspar. Exceptionally wide dikes are mined by underground methods after a moderate depth is reached by opencut methods.

Hand cobbing and sorting are employed at all small mines and at some large ones, not only to upgrade the feldspar but to select byproduct minerals such as mica and beryl before crushing; the smaller mines usually are worked intermittently. At the larger mines, crushers and picking belts are installed at the open pit, permitting the recovery of feldspar and associated minerals from ores that are too intimately mixed for hand cobbing.

Mining feldspar for subsequent treatment by flotation is simpler and cheaper than mining for other treatments, because mining need not be selective and fine fragmentation is not harmful. Most drilling is by wagon drills using 2½-inch bits, and larger rounds are blasted using 40 and 60 percent dynamite or ammonium nitrate. The ore is loaded by power shovels and transported by truck to the flotation plants.

Dragline excavators, loading bins, and trucks are used to recover feldspar from sand deposits.

Milling

Hand-cobbed or belt-picked ore is crushed, dried, and screened. Magnets are employed to remove tramp iron. The undersize goes first to mixing bins and then to silex-lined pebble mills for final grinding and sizing. Variations of this simplified flowsheet are in use.

In a typical North Carolina froth flotation plant (*7–8*), run-of-mine rock is reduced to minus 4 inches in jaw crushers and to ⅝ inch in gyratory crushers. The crushed rock goes to storage bins or to stockpiles from which millfeed is withdrawn as needed. Millfeed is wet-ground in rodmills in closed circuit with 10-mesh screens. Spiral classifiers are used to deslime the ore, the overflow going to waste. Deslimed pulp is conditioned with amine collectors, and most of the mica is removed by flotation in a rougher circuit. Some feldspar and quartz are floated with the mica at this point, and the froth product is recleaned to produce a salable mica byproduct. The pulp is again conditioned, and the heavy minerals in the feed (especially garnet, tourmaline, and hornblende) are floated, along with any remaining mica. This fraction is discarded.

Feldspar in the tailing from the heavy mineral scavenging circuit is froth-floated using an amine collector. The concentrate is cleaned, dried, and ground. The tailing from the final rougher circuit may be marketed as structural sand, or further purified and sold as glass sand.

Separation of feldspar from sand deposits requires only froth flotation and magnetic sepa-

ration without preliminary crushing.

The precentage of feldspar produced by each milling method is shown in table 1.

TABLE 1.—*Derivation of ground feldspar, by percent*

Year	Hand cobbed	Flotation concentrate	Feldspar-silica mixtures
1959	31	53	16
1960	30	55	15
1961	23	62	15
1962	23	66	11
1963	17	66	17

Electrostatic separation has been attempted on a commercial scale, but although technically feasible it was too expensive in the area where it was used. Recent articles indicate that research on electrostatic separation of feldspar in the U.S.S.R. has shown promise (*9*).

USES

Glass consumed about 56 percent; pottery, 30 percent; and enamel, 5 percent. Other ceramic uses and scouring soaps and powders accounted for the next largest percentages.

A small tonnage of carefully selected crude material was consumed in the manufacture of teeth for dentures. Small quantities also were used as a binder in grinding wheels and as a soil conditioner.

Poultry grit and roofing granules formerly accounted for 20 percent of the feldspar consumed but only minor quantities now go to these uses.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Quartz and mica are important byproducts of the feldspar industry. Some feldspar mines were first worked for sheet mica. Feldspar flotation and electrostatic separation methods produce glass-grade quartz, an ideal byproduct, since quartz and feldspar are used by the same industries. Other accessory minerals of feldspar that have been marketed are amblygonite, beryl, cassiterite, columbite, hubnerite, lepidolite, pollucite, spodumene, tantalite, and wolframite. Gem stones seldom constitute a byproduct in the larger feldspar mines because large-scale operations normally destroy gem materials. In the smaller operations where hand cobbing and sorting are used, production of gem stones may be important. Some varieties of feldspar have been used for ornamental building stone and art objects.

ALTERNATE MATERIALS

Until 1930 imported Cornwall stone was the only competitor for domestic feldspar in the ceramic industry. There are now a large and growing number of alternate materials. Among these are nepheline syenite, aplite, talc, pyrophyllite, electric furnace slag, and lithospar.

Nepheline syenite is a granular igneous rock made up of nephelite ($K_2O \cdot 3Na_2O \cdot 4Al_2O_3 \cdot 9SiO_2$), potash feldspar (microcline), soda feldspar (albite), and minor accessory minerals such as mica, hornblende, and magnetite. Nepheline syenite permits lower firing temperatures and has been used in sanitary-ware bodies, floor and wall tile, electrical porcelain, vitreous bodies, glass, and porcelain enamels.

Aplite is a rock product, commercially mined in Virginia, composed principally of albite, zoisite, and sericite. It is used in container and flat glass batches.

Talc can replace feldspar primarily in dinnerware and wall-tile bodies. Pyrophyllite is used as a source of alumina in enamels and wall-tile bodies.

Electric furnace slag, a byproduct in the manufacture of elemental phosphorus, is used as a low-cost source of alumina in glass batches where color is not a prime consideration.

Lithospar is a naturally occurring mixture of spodumene and feldspar. It is used as a flux since the fusion temperature is much lower than that of either constituent alone.

Plastics have become prominent as replacements for dinnerware, tile, and other ceramic products containing feldspar. Aluminum tile is increasingly used in place of ceramic wall tile.

SECONDARY SOURCES AND RECOVERY

The most important secondary source of feldspar is scrap glass. The only other secondary source is garspar, the intimate mixture of finely ground glass and quartz produced by grinding and polishing plate glass with silica sand. It contains about 15 percent glass and 85 percent silica and consists mostly of minus 325-mesh materials.

RESERVES

Adequate resources of feldspathic ores exist in pegmatite bodies in the United States to provide for feldspar requirements for hundreds of years, but quantitative data are lacking. The largest developed areas in the East are the Spruce Pine district in North Carolina, the Keene and Grafton districts in New Hampshire, the Paris-Rumford and Topsham districts in

Maine, and the Middletown district in Connecticut. In the West, South Dakota has large areas of pegmatite occurrences in Custer and Pennington Counties, and in Colorado the Front Range has pegmatites over several hundred square miles. Large deposits of California beach sands in Monterey Bay contain about 50 percent feldspar.

Quantitative data on world reserves of feldspar are not available. The same general conditions hold true for foreign countries as for the United States. Vast resources are available from feldspathic rocks and sands in many parts of the world. Large commercial resources of feldspar occur in Canada. According to reports, 7.6 million tons of ore containing 59.2 percent feldspar has been blocked out on a 25-acre tract at Cape Feldspar, Quebec.

SOURCES OF STATISTICAL INFORMATION

Annual data on production and sales of crude feldspar are obtained from a canvass of domestic producers by the Bureau of Mines, and annual data on ground feldspar sold, on shipments by destination, and on uses are obtained by the Bureau from all known merchant mills in the United States. No canvass of users is made.

World production and trade data are also compiled by the Bureau. U.S. exports and imports are compiled from data supplied by the U.S. Department of Commerce.

PRODUCTION, CONSUMPTION, AND TRADE

The United States has been the world's leading producer and consumer of feldspar for about 70 years. In 1959–63, the United States accounted for 35 percent of world production. In 1959–63 the glass, pottery, and enamel industries consumed 90 percent of the ground feldspar sold by merchant mills (table 2). Table 3 shows the amount of feldspar shipped from U.S. mills in this period.

TABLE 2.—*Ground feldspar sold by merchant mills in the United States, by uses*

[Short tons]

Year	Glass	Pottery	Enamel	Other [1]	Total
1959	305,188	183,261	23,305	37,460	549,214
1960	315,313	166,052	36,929	41,811	560,105
1961	294,682	152,551	25,149	55,966	528,348
1962	321,563	152,028	21,172	46,863	541,626
1963	293,257	147,166	27,391	59,533	527,347
1964	313,187	195,510	24,068	65,941	598,706

[1] Includes soaps, abrasives, and other ceramic and miscellaneous uses.

TABLE 3.—*Ground feldspar shipped from merchant mills in the United States*

[Short tons]

Destination	1959	1960	1961	1962	1963
California	87,332	91,452	99,149	79,075	78,164
Illinois	57,952	54,089	55,815	46,283	49,822
Indiana	34,212	28,426	39,700	19,139	20,688
Maryland	17,572	16,017	14,092	11,748	11,636
Massachusetts	4,229	5,101	6,235	4,603	4,231
New Jersey	28,577	25,989	38,245	53,640	62,336
New York	16,463	19,701	16,850	21,696	23,631
Ohio	71,293	67,324	67,304	76,287	122,242
Pennsylvania	56,332	60,907	55,947	34,843	40,567
Texas	22,057	21,440	22,994	22,502	(1)
West Virginia	51,965	36,216	27,384	(1)	18,714
Wisconsin	10,823	9,677	8,727	(1)	(1)
Other destinations [2]	101,298	92,009	89,184	157,531	166,675
Total	560,105	528,348	541,626	527,347	598,706

[1] Included with "Other destinations."

[2] Includes Alabama (1960–62), Arkansas, Colorado, Connecticut, Florida (1960–61), Georgia (1960 and 1963), Hawaii (1961), Kentucky, Louisiana, Maine (1959–60), Michigan, Minnesota, Mississippi, Missouri, Oklahoma, Rhode Island, South Carolina (1962–63), Tennessee, Utah (1960), Vermont (1960 and 1962–63), Virginia (1963), Washington (1959–62), shipments that cannot be separated by States, and shipments indicated by footnote 1. Also includes exports to Canada, Colombia (1961), Cuba (1959–60), England (1959 and 1962), Mexico, Panama, Philippines (1963), Puerto Rico (1959), and Venezuela (1959–63), and small quantities to other countries.

Owing to its wide distribution and low unit cost, feldspar has never been significant in world commerce. U.S. feldspar imports, essentially all from Canada, have declined from an annual average of almost 19,000 long tons during 1945–49 to about 4,000 tons per year in 1959–63. Tariff rates effective October 31, 1963, on feldspar were 12.5 cents per long ton on crude and 7.5 percent ad valorem on ground feldspar. World production of feldspar is shown in table 4.

TABLE 4.—*World production of feldspar, by countries* [1]

[Thousand long tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963
Brazil	(2)	[3] 34	[3] 39	[3] 39	[3] 39	[3] 39
France	71	79	84	96	119	[3] 98
Germany, West	157	175	264	265	270	[3] 270
Italy	50	60	85	93	91	100
Japan [4]	40	60	91	51	47	[3] 47
Norway	43	39	53	69	54	65
South Africa, Republic of	8	10	16	23	28	41
Sweden	49	46	55	56	[3] 56	45
United States (sold or used)	521	548	502	497	492	549
U.S.S.R.	(2)	[3] 185	[3] 195	[3] 205	[3] 205	[3] 210
Other countries	79	114	106	130	139	126
Total	1,210	1,350	1,490	1,530	1,540	1,590

[1] Feldspar is produced in China, Czechoslovakia, Republic of Korea, and Rumania, but data are not available; no estimates included in total except for Czechoslovakia.

[2] Data not available; estimate included in total.

[3] Estimate.

[4] In addition, the following quantities of aplite and other feldspathic rock were produced: 1954–58 (average), 72,871 tons; 1959, 88,451 tons; 1960, 91,339 tons; 1961, 132,041 tons; 1962, 168,543 tons; 1963, 211,172 tons.

PRICES AND COSTS

Crude feldspar prices do not appear in the trade publications. The average value of crude feldspar, computed from producers' reports to the Bureau of Mines in 1963, was $10.06 per long ton.

Feldspar prices were quoted in the E&MJ Metal and Mineral Markets in 1963 as follows:

North Carolina, bulk carlots, 200-mesh, $17 to $21 a short ton; 325-mesh $18 to $22, glass-grade feldspar $13.50; and 20-mesh semigranular $7.50 (add $3 a ton to bulk quotations for bags and bagging).

In 1963, computed from reports from merchant grinders to the Bureau of Mines, the average selling price of ground feldspar was $12.28 a short ton; the Illinois price was the highest, at $25.10.

TAXES

Producers of feldspar are granted a depletion allowance of 15 percent for both domestic and foreign production.

TRANSPORTATION

Feldspar is normally shipped by rail either in bulk or in 100-pound bags. Except for a few high-grade, high-value products it cannot be marketed far from its source because freight costs become excessive. Ocean shipping from Canada to the eastern seaboard commenced in 1957.

RESEARCH

Comprehensive studies have been made in recent years to obtain data concerning the effects of particle size of feldspar and quartz on processing characteristics and fired properties of porcelain and other ceramic bodies. New methods of processing feldspar ores have been developed, including methods for separating potash feldspars from soda feldspars. A number of new products requiring feldspar as a principal ingredient have been patented.

The Bureau of Mines has demonstrated the technical feasibility of recovering alumina from anorthosite and more recently has conducted beneficiation studies to determine the practicability of obtaining feldspar as a byproduct in processing pegmatites for recovery of beryl. A study was recently made by the Bureau on feldspar mining, processing, and marketing methods in the Eastern United States.

OUTLOOK

The principal outlets for feldspar are in the manufacture of glass, pottery, and enamel, so that the amount of feldspar produced reflects fluctuations in these industries and is further affected by the degree to which aplite and nepheline syenite are substituted in these applications. From consideration of projections of these influences and of historic trends it is expected that annual feldspar production, although at a relatively constant average level around 525,000 tons during the past decade, will increase to about 750,000 tons by 1980.

Flotation concentrates will continue to supply the major part of the feldspar and should account for about 75 percent of the total domestic output by 1980. Use of feldspar-silica mixtures should also increase at the expense of hand-cobbed material and should represent about 20 percent of the total feldspar produced by 1980. Hand-cobbed feldspar will probably constitute between 5 and 10 percent of the total.

Beneficiation methods should improve, and byproduct feldspar can be expected in increasing quantities from mining of other minerals in granitic and pegmatitic rock. Competition from aplite and nepheline syenite will continue in areas that can be served by producers in Virginia and in Ontario, Canada.

PROBLEMS

The feldspar industry faces a number of problems from factors that are beyond the control of the producers. The principal market for feldspar is the glass industry, which in turn is dependent on the automobile, construction, and container industries; changes or fluctuations in any of these are reflected in feldspar production.

Economic separation of the soda and potash feldspar components is an important problem because many ceramic users prefer the potash type in their body mixes. Removal of impurities, particularly those that affect the color or the melting point of the final products, is a continuing problem to the producers, because they must be able to furnish essentially the same quality product from year to year.

The small miner using hand-cobbing methods has the dual problem of increasing labor costs and price competition from flotation products. As a consequence the smaller producers are being forced out of business.

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FERROALLOYS

By Gilbert L. DeHuff [1]

FERROALLOYS give various alloy steels their respective qualities, or serve important functions in the production of steel itself. The ferroalloy industry is closely associated with the iron and steel industry, its largest customer. The value of ferroalloy shipments for both 1962 and 1963 was about $390 million with tonnages approximating 2 million short tons annually. Approximately 30 companies engage in the production of ferroalloys, although some of these firms only produce ferroalloys as byproducts.

The principal ferroalloys are those of manganese and those of silicon. Manganese is used in the production of virtually all steel, primarily to neutralize the harmful effects of sulfur. Silicon is used primarily for deoxidization. Silicon and manganese have important alloying effects, also. Boron, chromium, cobalt, columbium, copper, molybdenum, nickel, phosphorus, tantalum, titanium, tungsten, vanadium, and zirconium are among the other elements contributing to the character of the various alloy steels.

One of the more important effects that these alloying elements impart is hardenability, or the depth to which the steel hardens. It has been determined that the use of a variety of alloying components increases hardenability at a greater rate than will equal additions of only one.

The principal information regarding the various ferroalloy elements is given in the respective commodity chapters of this volume. This chapter considers the interrelationships of the ferroalloys and the other aspects of the ferroalloying elements that cannot be covered adequately by individual commodity chapters.

BACKGROUND

The modern steel and ferroalloy industries began with Sir Henry Bessemer's discovery of the Bessemer process for making steel (1856). This was soon followed by Robert Mushet's introduction of manganese to make a sound, workable ingot. Manganese was virtually the only ferroalloying element used as an additive until the mid-1890's when ferrosilicon began to be used as a deoxidizer in place of ferromanganese. At about this time, the electric arc furnace was developed and applied to the production of ferroalloys. Among the first alloys to be made commercially in the electric furnace were ferrovanadium, ferrochromium, ferrotungsten, ferromolybdenum, and ferrosilicon.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

The ferroalloy industry is composed of approximately 30 companies. Two of these companies, Bethlehem Steel Co. and United States Steel Corp., are significant producers of blast-furnace manganese ferroalloys, in addition to being major steel producers. Although both companies produce ferromanganese primarily to satisfy the demands of their own steel plants, both companies sell the alloy to others. As may be seen from table 1, few of the 30 firms making ferroalloys approach a full range of the alloying elements among their products. The eight ferrophosphorus producers make ferrophosphorus only as a byproduct of their operations for the production of elemental phosphorus. They make no other ferroalloys.

Most of the domestic industry capacity is at plants east of the Mississippi River at points which are strategically situated with respect to consuming steel centers, cheap electric power, and favorable transportation.

Many foreign countries produce ferroalloys. While this industry formerly was confined chiefly to the large steel producing countries, in recent years the production from nations better known as producers of ferroalloying ore has become significant.

[1] Commodity specialist.

TABLE 1.—*Producers of ferroalloys in the United States in 1963*

Producer	Plant location	Product [1] and type of furnace [2]
The American Agricultural Chemical Co	Pierce, Fla	FeP (E).
Bethlehem Steel Co	Johnstown, Pa	FeMn (B).
Central Farmers Fertilizer Co	Georgetown, Idaho	FeP (E).
Chromium Mining and Smelting Corp., Ltd	Riverdale, Ill	FeCr (E).
Climax Molybdenum Co	Langeloth, Pa	FeMo (T).
FMC, Corp., Mineral Products Division	Pocatello, Idaho	FeP (E).
The Hanna Furnace Corp	Buffalo, N.Y	Silvery iron (B).
Hana Nickel Smelting Co	Riddle, Oreg	FeSi, FeNi (E).
Hooker Chemical Corp	Columbia, Tenn	FeP (E).
Interlake Iron Corp	Beverly, Ohio	SiMn, silvery iron, FeSi, FeCr (E).
Do	Toledo, Ohio	Silvery iron (B).
Jackson Iron & Steel Co	Jackson, Ohio	Silvery iron (B).
Keokuk Electro-Metals Co., Division of Vanadium Corporation of America.	Keokuk, Iowa	Silvery iron, FeSi (E).
Do	Wenatchee, Wash	FeSi (E).
E. J. Lavino & Co	Sheridan, Pa	FeMn (B).
Manganese Chemcials Corp	Kingwood, W. Va	FeMn [3].
Molybdenum Corporation of America	Washington, Pa	FeMo (E) and (T); FeW, FeB,FeCb (E).
Monsanto Chemical Corp	Soda Springs, Idaho	FeP (E).
Do	Columbia, Tenn	FeP (E).
Montana Ferro-Alloys Co., Inc	Woodstock, Tenn	FeMn, SiMn, FeSi, FeCr (E).
The New Jersey Zinc Co	Palmerton, Pa	Spln (E).
Ohio Ferro-Alloys Corp	Brilliant, Ohio	FeSi, FeCr (E).
Do	Philo, Ohio	FeMn, SiMn, FeSi, other [4] (E).
Do	Powhatan Point, Ohio	FeSi (E).
Do	Tacoma, Wash	FeSi (E).
Pittsburgh Metallurgical Co	Niagara Falls, N.Y	FeMn, SiMn, silvery iron, FeSi, FeCr (E)
Do	Calvert City, Ky	FeMn, SiMn, silvery iron, FeSi, FeCr (E).
Do	Charleston, S.C	FeSi, FeCr (E).
Reading Alloys Co., Inc	Robesonia, Pa	FeW, FeV, FeCb, other [4] (T).
Shieldalloy Corp	Newfield, N.J	FeTi, FeV, FeB, FeCb, FeCbTa (T).
Tennessee Products & Chemical Corp	Chattanooga, Tenn	FeSi, FeCr, (E).
Do	Rockwood, Tenn	FeMn, SiMn, FeSi, FeCr (E).
Tennessee Valley Authority	Muscle Shoals, Ala	FeP (E).
Tenn-Tex Alloy & Chemical Corp	Houston, Tex	FeMn, SiMn (E).
Titanium Alloy Manufacturing Division, National Lead Co	Niagara Falls, N.Y	FeTi, other [4] (E).
Union Carbide Corp., Metals Division	Niagara Falls, N.Y	FeCr, FeTi, FeW, FeV, FeB, FeCb, other [4] (E).
Do	Alloy, W. Va	FeMn, SiMn, FeSi, FeCr, FeZr (E); FeV (T).
Do	Marietta, Ohio	FeMn, SiMn, Spln, FeSi, FeCr (E).
Do	Ashtabula, Ohio	FeMn, SiMn, FeSi (E).
Do	Sheffield, Ala	FeMn, SiMn, FeSi (E).
Do	Portland, Oreg	FeMn, SiMn, FeSi (E).
United States Steel Corp	Birmingham (Ensley-Fairfield), Ala	FeMn (B).
Do	Duquesne, Pa	FeMn (B).
Vanadium Corporation of America	Cambridge, Ohio	FeTi, FeV, FeCb, other [4] (E).
Do	Vancoram, Ohio	FeSi, FeCr, other [4] (E).
Do	Graham, W. Va	FeMn, SiMn, FeSi, FeCr, other (E).
Victor Chemical Division, Stauffer Chemical Co	Mt. Pleasant, Tenn	FeP(E).
Virginia-Carolina Chemical Corp	Nichols, Fla	FeP (E).
Do	Charleston, S.C	FeP (E).
Woodward Iron Co	Woodward, Ala	FeSi (E).

[1] FeMn, ferromanganese; Spln, spiegeleisen; SiMn, silicomanganese; FeSi, ferrosilicon; FeP, ferrophosphorus; FeCr, ferrochromium; FeMo, ferromolybdenum; FeNi, ferronickel; FeTi, ferrotitanium; FeW, ferrotungsten; FeV, ferrovanadium; FeB, ferroboron; FeCb, ferrocolumbium; FeCbTa, ferrocolumbium-tantalum; FeZr, ferrozirconium.

[2] E–Electric; B–Blast; T–Thermite.

[3] Made by fused salt electrolysis.

[4] Includes Alsifer, simanal, ferrosilicon boron, and miscellaneous ferroalloys.

DEFINITIONS OF TERMS, GRADES, AND SPECIFICATIONS

The term "ferroalloys" is defined by Webster's New International Dictionary of the English Language (1961) as "a crude alloy of iron with some other metal, used for deoxidizing molten steel and making alloy steels." In practice, however, the term is used loosely to include alloys or compounds containing little or no iron, and even relatively pure metals, employed to introduce additive or alloying elements in the production of steel. "Addition agent" is perhaps a more correct terminology for covering all three groups (*24*),[2] although not as freely employed. In using the term "ferroalloys" in the treatment of its statistics, the Bureau of Mines goes beyond the strict definition, following the sense of the general Webster definition of the prefix "ferro-" as denoting the "presence of, or connection with, iron."

The prefix "ferro-" used specifically as linked to a particular alloying element designates an alloy of that metal and iron; for example, ferromanganese, ferrosilicon, or ferrochromium. The various ferroalloys in general, and these three in particular, are offered in a wide variety of grades, some of which combine two of the alloying elements as in silicomanganese or in ferrochrome silicon. In the case of ferrosilicon, as the silicon content drops below 20 percent the resulting alloy is called ferrosilicon by some, silvery pig iron by others. The latter grades down into what is essentially a high-silicon pig iron. Spiegeleisen may be considered a low-manganese ferromanganese, or a

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

high-manganese pig iron. European practice frequently has been to use ferromanganese of lower manganese content than in the United States—alloy that would be termed "off-grade ferromanganese" in this country.

Industry specifications for 14 ferroalloys are presented by the American Society for Testing and Materials (ASTM) (*3*).

TECHNOLOGY

About two-thirds of the total U.S. production of ferromanganese is made in blast furnaces, the remainder is made in electric furnaces. Virtually all spiegeleisen was made in blast furnaces, until a principal producer completed conversion to electric furnaces in 1963. Silicomanganese, medium carbon, low carbon, and special grades of ferromanganese are made in the electric furnace, as are ferrosilicon and the various regular grades of ferrochromium. The lower grades of silvery pig iron are made in blast furnaces; the higher grades, sometimes considered to be among the ferrosilicons, may be made in either electric or blast furnaces. The other ferroalloys are made in electric furnaces or by the thermite process. Special processes, such as aqueous or fused salt electrolysis or special vacuum furnaces, are used by some producers for production of certain of the higher quality alloys.

The blast furnaces making ferroalloys are the same as those used for making pig iron or are similar to them with modifications favoring the alloy production. Although not the usual current domestic practice, a furnace might have a run of sufficient length to produce the quantity of alloy desired and then be returned to its normal business of pig iron production.

Electric arc furnaces used for making ferroalloys may be the same as those for making calcium carbide, although to use the same furnace for both is not good practice. Certain ferroalloys, however, may be produced interchangeably in one furnace, and the practice is not unusual.

Although high-carbon ferroalloys, such as high-carbon ferromanganese, are made in quantity in the electric furnace, these furnaces are essential for large quantity production of the medium- and low-carbon grades of alloy. Production of the lower carbon and other special grades of alloy may employ a two- or even three-stage furnacing operation, depending on the specifications desired and the raw materials used.

Some of the less common ferroalloys and their metals are made by the thermite (thermic or Thermit) process wherein aluminum powder or shot, or some other finely divided highly active metal, is mixed with the ore and ignited. The alloying element of the ore is reduced, the oxygen of the ore transfers to the reacting metal, and heat of the reaction melts the charge.

In the production of virtually all steels, a manganese ferroalloy is employed to counteract the harmful effects of sulfur. The manganese addition acts as a deoxidizer as well. General practice, however, adds a silicon alloy for this purpose, or another deoxidizer stronger than manganese. In certain instances, silicomanganese is used as one alloy to accomplish both objectives.

The different ferroalloying elements may be grouped according to some of their principal functions, although certain of these elements are seldom used for the purpose specified, because of cost or other reasons, and two of the elements—sulfur and phosphorus—are ordinarily considered harmful:

1. To deoxidize—Silicon, aluminum, manganese, calcium, vanadium, titanium, and zirconium. Although manganese additions contribute to deoxidization of steel, the element is not ordinarily added for this purpose.
2. To neutralize sulfur—Manganese. Titanium and zirconium are effective, but are not used because of cost, relatively limited supply, and metallurgical problems.
3. To improve hardenability—Aluminum, boron, chromium, manganese, molybdenum, nickel, silicon, tungsten, vanadium, and others. Hardenability is the depth to which the steel can be hardened. Effects are greatly increased by use of a combination of different elements.
4. To improve corrosion resistance—Chromium, columbium, nickel, phosphorus, silicon, molybdenum, titanium, tungsten, and copper.
5. For special magnetic or electrical properties—Silicon, cobalt, nickel, chromium, and tungsten.
6. For high temperature applications—Chromium, cobalt, columbium, molybdenum, nickel, titanium, tungsten, and vanadium.
7. To improve machinability—Lead, phosphorus, selenium, and sulfur.
8. To increase strength—Chromium, molybdenum, silicon, vanadium, nickel, phosphorus, columbium, and manganese.
9. To refine grain—Vanadium, and aluminum.
10. For toughness—Nickel, vanadium, manganese, and molybdenum (*1,2,12,24*).

In improving hardenability the alloying effects are increased by using a number of different alloying elements in combination, and the effect of any one element on the properties of steel can not be determined independently of the others. The multiplying factor principle

or method for calculation of hardenability is based on experiments by Grossmann and others. It states in effect that, when two or more alloying elements are present in a steel, the total hardenability is affected by the product and not the sum of the hardenability effects of the individual alloying elements. Because manganese and silicon are almost invariably present in heat-treatable engineering and constructional steels, and both exhibit significant alloying effects although not necessarily added for that purpose, they must also be considered in any application of the formula developed by Grossmann (*1*, *11*, *14*, *16*, *24*).

An excellent example of the effects of the multiple-alloy principle was illustrated in the nickel-chromium-molybdenum steels widely adopted for engineering use during World War II. These steels, identified as the American Iron and Steel Institute (AISI) 8600 series, were known as triple-alloy steels although carrying 0.87 percent manganese and 0.28 percent silicon in addition to the nickel, chromium, and molybdenum percentages of 0.55, 0.50, and 0.20, respectively. The manganese and silicon were added to control sulfur and oxygen, but their alloying effect exceeds that of the three other elements combined.

It is not uncommon for six, seven, or eight different alloying elements to be included in the specifications for heat-treatable steels.

USES

The ferroalloys proper are used principally in the production of steel. In this context, they can be grouped in two more or less arbitrary categories: (1) those finding appreciable use in the production of carbon as well as alloy steels; and (2) those used solely or primarily in the production of alloy steels. The members of the first group may be important for the production of particular alloy steels, and some from the second group may occasionally be used in producing carbon steel.

The ferroalloys and the ferroalloy elements are also used by iron foundries, and by the nonferrous metal, chemical, and miscellaneous industries. Uses by the iron foundries are somewhat similar to those of the steel industry. The nonferrous metal, chemical, and miscellaneous industries tend to use a lesser proportion of the total as true ferroalloys, and more as compounds, master alloys (nonferrous), and metals of various degrees of purity. Among the more important uses outside the iron and steel industry are those for producing nonferrous high-temperature alloys, cryogenic alloys, magnet alloys, welding rods and coatings, cutting and wear-resistant materials, and for strengthening and hardening aluminum.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

All ferrophosphorus is produced as a byproduct resulting from the production of elemental phosphorus. Production of the alloy continues to exceed demand, creating an accumulation of large stocks. These stocks totaled 221,000 short tons at the end of 1963.

There are some limited coproduct relationships between other ferroalloys and base metals through the intimate association of the respective elements in a few ores.

CONSERVATION

From the discussion of technology, it can be seen that the steelmaker frequently has a choice of addition agents to achieve the effects desired. Under normal conditions, the choice is narrowed by cost, but in times of emergency short supply of one element often can be overcome by use of another. An exception is the use of manganese to counteract the effects of sulfur, and no satisfactory substitute has yet been found for it in the commercial production of steel in large quantities. Some conservation of manganese, estimated at not more than 5 or 10 percent, can be achieved by careful control of the production operation, if emphasis is not placed on costs.

SOURCES OF STATISTICAL INFORMATION

The Bureau of Mines annually collects production, shipment, and stock information from the ferroalloy producers on a voluntary basis. Data on consumption of all the common ferroalloys has been collected by the Bureau since January 1, 1959, on a monthly basis. In doing so, the iron foundries, nonferrous metal, chemical, and miscellaneous industries are covered in addition to the steel industry.

U.S. import and export statistics are compiled by the Bureau of the Census from data filed by the importer or the exporter with the Bureau of Customs. Foreign production data, not always readily available, are obtained annually by the Bureau of Mines from questionnaires sent to U.S. Consular offices abroad, whose principal sources of information are the official statistical releases of the particular foreign governments concerned. In many instances, the ferroalloys data are grouped together in one total rather than being treated individually.

PRODUCTION, CONSUMPTION AND TRADE

The domestic production and consumption of ferroalloys, as measured by shipments, vary with the production of steel ingots. Production and shipments are shown in table 2; consumption in tables 3 and 4.

Imports for consumption of ferroalloys are detailed in table 5; exports in table 6. Imports for a few of the ferroalloys in some years have been substantial in comparison with consumption. For certain years U.S. Government acquisitions under the Department of Agriculture's program for barter of surplus U.S. agricultural materials have been responsible for an appreciable portion of the larger quantities.

High-carbon ferromanganese was the largest ferroalloy import item in both quantity and value in 1949–63, except that in 1959 high-carbon and low-carbon ferrochromium both surpassed it in value. Medium-carbon ferromanganese, ferrosilicon, and silicomanganese are the only other ferroalloy imports that exceeded 10,000 tons in any year of the 1959–63 period.

TABLE 2.—*Ferroalloys produced and shipped from furnaces in the United States*

Alloy	1962				1963			
	Production		Shipments		Production		Shipments	
	Gross weight (short tons)	Alloy element contained (average percent)	Gross weight (short tons)	Value (thousands)	Gross weight (short tons)	Alloy element contained (average percent)	Gross weight (short tons)	Value (thousands)
Ferromanganese [1]								
Blast furnace	528,183	76.76	483,181	$86,694	468,438	76.67	522,526	$77,965
Electric furnace	252,929	78.05	244,515	47,652	[2] 282,760	[2] 78.06	[2] 279,587	[2] 47,111
Total	781,112	77.18	727,696	134,346	751,198	77.19	802,113	125,076
Silicomanganese	136,197	65.82	129,925	25,429	151,590	65.83	154,836	24,910
Ferrosilicon	419,741	54.99	398,731	70,971	439,074	55.72	448,008	76,555
Silvery iron:								
Blast furnace	84,636	9.70	102,250	7,580	61,549	9.49	68,904	5,048
Electric furnace	133,751	15.76	136,589	11,513	132,628	17.34	133,172	11,005
Total	218,387	13.41	238,839	19,093	194,177	14.86	202,076	16,053
Chromium alloys:								
Ferrochromium [3]	191,302	65.08	173,959	63,111	231,741	66.08	235,374	63,962
Other chromium alloys [4]	70,257	39.93	71,004	17,957	82,469	38.85	79,352	18,260
Total	261,559	58.32	244,963	81,068	314,210	58.93	314,726	82,222
Ferrotitanium	2,572	22.55	2,440	1,727	2,889	26.27	3,058	2,536
Ferrophosphorus	96,655	24.08	51,650	2,735	102,028	23.93	77,827	2,877
Ferrocolumbium and ferrotantalum-columbium	1,351	58.25	1,342	5,285	1,356	58.11	1,256	4,990
Ferronickel	19,910	53.08	19,678	50,107	21,807	49.18	22,208	53,207
Other [5]	61,470	27.75	60,803		35,055	36.09	61,970	
Grand total	1,998,954	57.90	1,876,067	390,761	2,013,384	58.99	2,088,078	388,426

[1] Includes briquets.
[2] Includes fused salt electrolytic.
[3] Includes low- and high-carbon ferrochromium and chromium briquets.
[4] Includes ferrochrome-silicon, exothermic chromium additives, and other chromium alloys.
[5] Includes Alsifer, ferroboron, ferromolybdenum, ferrotungsten, ferrovanadium, simanal, spiegeleisen, zirconium-ferrosilicon, ferrosilicon-zirconium, aluminum-silicon alloy, and other miscellaneous ferroalloys.

TABLE 3.—*Consumption by end uses of ferroalloys as additives in the United States in 1963*

[Short tons, gross weight]

Alloy	Stainless steels	Other alloy steels [1]	Carbon steels	Tool steels	Gray and malleable iron castings	Miscellaneous uses	Total
Ferromanganese [2]	11,470	149,441	747,909	3,859	29,174	15,641	957,494
Silicomanganese	6,276	38,317	93,247	1,005	3,677	1,566	144,088
Silicon alloys [3]	15,829	88,365	133,089	1,324	320,938	92,083	651,628
Ferrotitanium	279	1,048	723	59		146	2,255
Ferrophosphorus	15	3,461	8,036		927	72	12,511
Ferroboron	7	46	146		12	19	230
Total	33,876	280,678	983,150	6,247	354,728	109,527	1,768,206

[1] Includes steel mill rolls.
[2] Includes spiegeleisen, manganese metal, and briquets.
[3] Includes silicon metal and silvery iron.

TABLE 4.—*Consumption by end uses of ferroalloys as alloying elements in the United States in 1963*

[Short tons of contained element]

Alloy	Stainless steels	Other alloy steels	Carbon steels	High speed steels	Other tool steels [1]	Gray and malleable iron castings	High temperature alloys	Miscellaneous uses	Total
Ferrochromium [2]	127, 766	[3]45, 550		1, 064	1, 685	3, 666	5, 258	1, 826	186, 815
Ferromolybdenum [4]	1, 027	[5]1, 007		323	184	1, 417	135	463	4, 556
Ferrotungsten		[5]119		306	145		29	8	607
Ferrovanadium	32	[6]1, 500	246	279	184	17	16	28	2, 302
Ferrocolumbium	217	194	83	1			147	14	656
Ferrotantalum-columbium	8						4	5	17
Total	129, 050	48, 370	329	1, 973	2, 198	5, 100	5, 589	2, 344	194, 953

[1] Includes hot-work and die steels.
[2] Includes other chromium ferroalloys and chromium metal.
[3] Includes quantities believed used in producing high-speed and other tool steels and stainless steels, because some firms failed to specify individuals uses.
[4] Includes calcium molybdate and molybdenum silicide.
[5] Includes stainless steels, steel mill rolls, and other alloy steels.
[6] Includes steel mill rolls.

TABLE 5.—*U.S. imports for consumption of ferroalloys and ferroalloy metals*

Alloy	1962			1963		
	Gross weight (short tons)	Content (short tons)	Value	Gross weight (short tons)	Content (short tons)	Value
Calcium silicide	685	(1)	$200, 163	[2] 560	(1)	[2] $159, 575
Chromium metal	648	(1)	992, 655	861	(1)	1, 308, 120
Chromium-nickel and chromium-vanadium	3	(1)	3, 352			
Ferroboron	10	(1)	16, 032	11	(1)	17, 194
Ferrocerium and other cerium alloys	10	(1)	60, 421	8	(1)	48, 797
Ferrochrome and ferrochromium—						
Containing 3 percent or more carbon	12, 442	7, 685	2, 126, 286	6, 532	3, 961	1, 043, 275
Containing less than 3 percent carbon	24, 084	17, 229	7, 718, 646	22, 511	15, 984	5, 763, 649
Ferrochromium-tungsten, chromium-tungsten, chromium-cobalt-tungsten, tungsten-nickel, and other alloys of tungsten, n.s.p.f. (tungsten content)	(1)	21	47, 044	(1)	21	40, 290
Ferromanganese—						
Containing not over 1 percent carbon	1, 040	940	442, 434	628	560	252, 070
Containing over 1 and less than 4 percent carbon	12, 826	10, 517	2, 883, 891	15, 666	12, 581	2, 867. 241
Containing not less than 4 percent carbon	111, 748	85, 585	13, 430, 508	132, 336	102, 236	13, 854, 429
Ferromolybdenum, molybdenum metal and powder, calcium molybdate, and other compounds and alloys of molybdenum (molybdenum content)	(1)	39	189, 455	(1)	37	174, 267
Ferrosilicon	16, 329	2, 573	975, 892	13, 357	2, 376	743, 765
Ferrotitanium	120	(1)	87, 702	41	(1)	35, 145
Ferrotungsten	329	267	531, 071	546	441	608, 589
Ferrovandadium	88	(1)	231, 028	443	(1)	1, 186, 697
Manganese metal	(1)	1, 504	670, 601	[2] 2, 631	[3]	943, 902
Manganese silicon (manganese content)	(1)	17, 153	3, 049, 113	(1)	14, 429	2, 318, 003
Silicon metal (silicon content)	12	12	5, 015			
Tungsten in combinations, in lump, grains, or powder (tungsten content)	(1)	249	937, 950	(1)	42	163, 024
Tungstic acid and other alloys of tungsten, n.s.p.f. (tungsten content)	(1)	[4]	890	(1)	19	80, 595
Zirconium silicon	70	(1)	12, 999	30	(1)	5, 582

[1] Not recorded.
[2] Data known to be not comparable with earlier years.
[3] Effective Sept. 1, 1963, reported in gross weight. However, because gross weight and manganese content are almost the same, the total is tabulated here under gross weight.
[4] 356 pounds.

Source: Bureau of the Census.

TABLE 6.—*U.S. exports of ferroalloys and ferroalloy metals*

Alloy	1960		1961		1962		1963	
	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value
Ferrochromium	15,588	$5,248,750	7,844	$2,837,518	3,075	$1,182,382	2,354	$772,937
Ferromanganese	751	202,457	469	146,178	4,114	629,401	678	154,973
Ferromolybdenum	212	489,140	179	501,476	95	305,126	120	379,173
Ferrophosphorus	47,897	2,094,527	32,860	1,425,568	14,130	594,666	41,361	1,302,337
Ferrosilicon	5,501	867,140	34,764	6,104,913	4,101	1,348,661	3,130	947,773
Ferrotitanium and ferrocarbon-titanium	245	157,419	212	93,389	130	95,265	211	182,828
Ferrotungsten			(1)	1,569	6	26,136	1	2,927
Ferrovanadium	162	506,624	120	436,208	201	745,912	183	587,690
Other ferroalloys	3,845	846,888	4,839	1,234,682	348	233,591	430	262,985
Spiegeleisen	148	15,056	525	46,617	715	59,275	1,176	89,766
Total	74,349	10,428,001	81,812	12,828,118	26,915	5,220,415	49,644	4,683,389

[1] Less than 1 ton.

Source: Bureau of the Census.

The only consistently large export by tonnage from 1950–63 has been ferrophosphorus. In the 1959–63 period, however, the value of exported ferrochromium exceeded that for ferrophosphorus in every year except 1963. In 1961 and 1962, the value of exported ferrosilicon was more than either.

The ferroalloys carry a variety of duty rates. Some of these are summarized in table 7.

TABLE 7.—*U.S. tariffs for various ferroalloy items*

Item	Duty rate 1 [1]	Duty rate 2 [1]
Ferrochromium:		
Not over 3 percent carbon	8.5 percent ad valorem	30 percent ad valorem.
Over 3 percent carbon	0.625 cent per pound contained chromium	2.5 cents per pound contained chromium.
Ferrosilicon chromium	10 percent ad valorem	25 percent ad valorem.
Ferromanganese:		
Not over 1 percent carbon	0.6 cent per pound contained manganese plus 4.5 percent ad valorem.	1.875 cents per pound contained manganese plus 15 percent ad valorem.
Over 1 percent but not over 4 percent carbon	0.9375 cent per pound contained manganese	1.875 cents per pound contained manganese.
Over 4 percent carbon	0.625 cent per pound contained manganese	1.875 cents per pound contained manganese.
Silicomanganese	0.9375 cent per pound contained manganese plus 7.5 percent ad valorem.	1.875 cents per pound contained manganese plus 15 percent ad valorem.
Spiegeleisen	75 cents per ton	75 cents per ton.
Ferromolybdenum	20 cents per pound contained molybdenum plus 6 percent ad valorem.	50 cents per pound contained molybdenum plus 15 percent ad valorem.
Ferronickel	1.25 cents per pound	3 cents per pound.
Ferrophosphorus	12.5 percent ad valorem	25 percent ad valorem.
Ferrosilicon:		
Over 8 percent but not over 60 percent silicon	0.8 cent per pound contained silicon	2 cents per pound contained silicon.
Over 60 percent but not over 80 percent silicon.	1 cent per pound contained silicon	3 cents per pound contained silicon.
Over 80 percent but not over 90 percent silicon.	2 cents per pound contained silicon	4 cents per pound contained silicon.
Over 90 percent silicon	4 cents per pound contained silicon	8 cents per pound contained silicon.
Ferrotitanium and ferrosilicon titanium	10 percent ad valorem	25 percent ad valorem.
Ferrotungsten and ferrosilicon tungsten	42 cents per pound contained tungsten plus 12.5 percent ad valorem.	60 cents per pound contained tungsten plus 25 percent ad valorem.
Ferrovanadium	12.5 percent ad valorem	25 percent ad valorem.
Ferrozirconium	12.5 percent ad valorem	25 percent ad valorem.

[1] Duty rate 1 is applicable for most nations; duty rate 2 is applicable for U.S.S.R., mainland China, and certain other specified Communist countries.

Source: Tariff Schedules of the United States. Effective Aug. 31, 1963. U.S. Tariff Commission, TC Publication 112, 1963, pp. 262–263, 267–268.

STRATEGIC CONSIDERATIONS

The U.S. ferroalloy industry has capacity in excess of present demand for ferroalloys, and for the immediate future under a peacetime economy. However, some of this capacity consists of outmoded plants and equipment which competition may force to close. Conceivably, under emergency conditions, the demand for certain alloys could tax the industry's ability to produce.

In its stockpiling program, the Government has established objectives for the following true ferroalloys: High-carbon, low-carbon, and silicon ferrochromium; ferrocolumbium; ferrotantalum columbium; high-carbon, and medium-low-carbon ferromanganese; silicomanganese; ferromolybdenum; ferrotungsten; and ferrovanadium.

In addition to stocks of ferroalloys, ample Government stocks of the most strategic ferroalloy ores or concentrate have been acquired.

With a few exceptions, notably ferrosilicon and ferromolybdenum, the United States depends on foreign sources of supply for raw materials. For those alloy stocks below the objectives, the deficiencies will be met by upgrading the raw materials held.

TABLE 8.—*Ferroalloys in Government inventories, June 30, 1964*

[Short tons]

	National (strategic stockpile)	CCC stocks and supplemental stockpile	Total
High-carbon ferrochromium	126,171	260,081	386,252
Low-carbon ferrochromium	127,740	188,647	316,387
Silicon ferrochromium	25,643	32,715	58,358
Ferrocolumbium	[1] 224		[1] 224
Ferrotantalum columbium	[1] 52		[1] [2] 70
	[2] 18		
High-carbon ferromanganese	142,739	766,374	909,113
Ferromolybdenum	[3] 2,013		[3] 2,013
Ferrotungsten	[4] 826		[4] 826
Ferrovanadium	1,765		1,765

[1] Contained columbium.
[2] Contained tantalum.
[3] Contained molybdenum.
[4] Contained tungsten.

PRICES

In the ferroalloy pricing, there is for most items a fairly wide price range depending upon sizing, quantity, and method of packaging. This is in addition to the differences attributable to the different grades of alloy as determined by analysis or other special features. Ferroalloy prices are subject to rather wide fluctuations, but usually the price changes are selective. However, a price change for one alloy may affect prices of others.

The price relationships among several of the alloys may be obtained from table 9. Actual prices in many instances as quoted are nominal.

TABLE 9.—*Ferroalloy prices for bulk quantities, December 1963*

Ferroalloy	Grade	Dollars per pound
Ferrochromium	High carbon	[1] 0.19
Ferrochromium	Standard low carbon, 67 to 73 percent chromium.	[1] .225
Ferrocolumbium	50 to 60 percent columbium	[1] 3.00
Ferromanganese	Standard high carbon	.085
Silicomanganese	Maximum 1½ percent carbon	.078
Spiegeleisen	19 to 21 percent manganese	.038
Ferromolybdenum	55 to 65 percent molybdenum, powdered.	[1] 1.95
Ferrophosphorous	24 percent phosphorous	.054
Ferrosilicon	50 percent silicon	[1] .121
Ferrotitanium	Low carbon	[1] 1.35
Ferrotungsten	70 to 80 percent tungsten	[1] 1.75
Ferrovanadium	Open hearth, 50 to 55 percent vanadium.	[1] 2.85

[1] Per pound contained significant element.

TRANSPORTATION

Most ferroalloy plants are near consuming centers and transportation of the finished product seldom presents a problem. Only for those plants in the Western States near ore sources would the transportation costs seriously limit the market area. In past emergencies the transportation of foreign ores has posed a serious problem. Hopefully, the subsequent location of U.S. Government stockpiles near consuming centers has solved this problem for the United States.

RESEARCH

Research on ferroalloys is conducted by members of the ferroalloy industry, steel companies, and the Bureau of Mines. These organizations have cooperated in steel research, benefiting both industries. Their research activities have led to reduction of steelmaking costs, reduction of ferroalloy production costs, development of new alloys, and the improvement of processes and products. Research plays a prominent role in the relative competitive position of the various alloys.

Much of past Bureau of Mines research has been concerned with the development of procedures for utilizing low-grade or off-grade domestic ores for the production of standard or special alloys. The Bureau is interested in basic research, however. Both the Bureau of Mines and private industry have endeavored to find a substitute for manganese to counteract the effects of sulfur, but the only probable substitutes have more disadvantages than manganese—problems of both supply and metallurgy which make them unattractive for commercial use on a large scale.

OUTLOOK

Growth of the ferroalloy industry roughly parallels that of steel. Individual ferroalloys fluctuate in demand due to the interchangeability of many of the ferroalloys, but majority of the output will continue to be the alloys of manganese and silicon.

More ferroalloy research will be necessary to produce the best ferroalloy at the least cost for the specific needs created by the increasingly wider variety of alloy steels and new technological developments in steelmaking.

To meet this challenge, the industry will continue to replace its less efficient, high-cost plants with the most modern automated equipment and methods.

PROBLEMS

Perhaps the most serious problem of the ferroalloy industry is limited control over its own fortune because of dependence on the steel industry.

Many ferroalloys are produced in electric furnaces and the producers make long-term electric power contracts to obtain favorable power costs. This leads to overproduction at times of low demand for the ferroalloy product, or relatively high fixed charge for an idle plant.

Overcapacity is a worldwide problem, resulting in keen competition for the world's markets. The emergence of relatively undeveloped ore-producing countries as producers of alloys has aggravated the problem. Domestically, however, overcapacity can be misleading in part since inefficient, outmoded plants and equipment are maintained in standby condition because of existing power contracts or in anticipation of a surge in demand.

Low-profit margins result from the lower prices needed by the domestic producer to meet the competition for restricted markets from foreign imports, in addition to his domestic competition. These low-profit margins limit funds for research and engineering development required for the growth of the industry.

The keen competition, together with the highly specialized operation combining art and science needed to manufacture ferroalloys, results in a lack of published technological information. This slows the advance of ferroalloy technology.

The industry's trained personnel, both professional and nonprofessional, acquire valuable skills. When such personnel are lost, replacements must be trained which requires time.

Certain alloys deteriorate in storage over a period of years causing stockpiling problems. Knowledge concerning behavior of the different alloys under various conditions of long-term stocking is spotty, inconclusive, or completely lacking. The question of stockpiling ferroalloys is also difficult because changing technology and its effects are hard to foresee. Hence, there is a problem in deciding the quantity and kind of alloy to be stocked, or whether a particular commodity should be stored in alloy form at all. If stocks are held only as ore, then insufficient processing capacity or the concentration of productive capacity in likely enemy target areas becomes a problem of supplying the needed alloy in time of emergency.

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FLUORINE

By Paul M. Ambrose [1]

FLUORINE is used in one ore form, fluorspar (CaF_2), mainly in the steel, glass, and enamel industries; in its principal acid form hydrofluoric acid (HF), for the manufacture of aerosols, refrigerants, and plastics; and in a natural and manufactured form, cryolite ($3NaF \cdot AlF_3$), as a flux in the electrometallurgy of aluminum.

Fluorite (CaF_2), commonly known in commerce by its rock name fluorspar, is the principal fluorine bearing mineral. Natural cryolite (Na_3AlF_6) has a higher fluorine content, but its occurrence is almost unique. The only known deposit of commercial tonnage is at Ivigtut, Greenland, and the total supply is relatively small. Phosphate rock often contains 2.5 to 3.5 percent fluorine and is potentially a large source.

Although the United States has been the world's largest fluorspar producer, domestic consumption far exceeds output, and over half the supply is imported. Most of the fluorspar produced in the United States is mined in an area along the Ohio River in southern Illinois and western Kentucky. This district also contains most of the domestic reserve. Capacity in the West has increased in recent years, particularly in Montana and Nevada, and in the future a larger portion of domestic output is expected to be produced in this area. Italy, Mexico, and Spain are the principal foreign sources.

In 1963, the largest use of fluorspar was for production of hydrofluoric acid which in turn was used as a catalyst in the production of high-octane gasoline. Hydrofluoric acid was also used to produce synthetic cryolite, aluminum fluoride, and many other fluorine compounds, including fluorocarbons for aerosols, refrigerants, and plastics. The second largest use of fluorspar was as a flux in steelmaking by the basic open-hearth, electric-furnace and basic oxygen methods. The third major use was in the manufacture of glass and enameled products. There are no adequate substitutes for fluorine in any of its major industrial uses.

Potentially a large alternative source of fluorine exists in wastes evolved in processing phosphate rock to produce fertilizers and other phosphate products, but to date commercial recovery of fluorine from phosphate rock in forms suitable for widespread industrial use has been on a relatively small scale.

The outlook is for increased consumption of fluorspar, particularly as a source of fluorine for the chemical industry and as a slag thinner in making steel. A long-range expansion in domestic output also may occur, but producers are confronted with major cost and quality problems in competing in the present market.

Some producers in the Illinois-Kentucky district must pump large quantities of water from the mines, adding substantially to production costs. Other problems include the need for more efficient recovery at reduced costs, increased recovery of byproducts, processes for utilizing lower grade and complex ores, the development of wider markets for flotation concentrates, and the need for additional information on resources.

BACKGROUND

Fluorspar has been known for centuries and was first used for ornamental slabs and ornaments that were carved from large crystals. Its usefulness as a flux was known in the 16th century. Mining started in England about 1775 and in the United States after 1820. There was substantial production before 1900 following the introduction of the basic open-hearth furnace in the steel industry. Production and usage increased with the growth of the steel industry and the introduction of a series of fluorocarbons useful as aerosols and refrigerants. Some of the fluorocarbons can be polymerized to make plastics.

[1] Commodity specialist.

The Illinois-Kentucky district has been the largest producer of fluorspar in the world but production for U.S. consumption has been surpassed by output from foreign sources, mostly from Mexico.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

There are approximately 26 fluorspar mines in the United States and about 11 mills. Most domestic production is contributed by about six companies having both mines and mills. Over half of the independent mines are small operations, producing only a few hundred tons a year which are sold to firms that operate mills or infrequently to consumers either directly or through brokers. The major independent and captive producers often supplement their mill requirements with ore purchased from small operators. Most of the domestic fluorspar operators are independent operators; however, in the acid segment of the industry there are three major firms that produce for their own consumption and one firm in the metallurgical phase of the industry. In 1963 the three firms accounted for about 64 percent of the total acid-grade output. Shipments of domestic fluorspar in 1963 totaled 200,000 tons valued at $9 million.

In the United States a small area in Hardin County, Ill., along the Ohio River accounted for about 66 percent of the total domestic shipments in 1963. Smaller tonnages were shipped from mines or mills in Colorado, Kentucky, Montana, Nevada, and Utah. Mills in Delaware and Texas processed foreign material. Principal producers of crude and finished fluorspar in the United States during 1963 are shown in table 1.

Production of fluorspar in Canada is centered chiefly in the St. Lawrence district on the Burin Peninsula in the Province of Newfoundland. There is a small fluorspar output from the Madoc area in Ontario.

The fluorspar mines in Mexico are scattered widely in the States of Chihuahua, Coahuila, Durango, Guerrero, Mexico, San Luis Potosi, and Sonora. A large part of the fluorspar has been produced by hand labor chiefly from surface workings, and has been hand sorted to yield a premium product. However, since about 1950, flotation plants and heavy-medium units have been installed by American organizations.

The fluorspar deposits in West Germany are in Baden and Bavaria. The mines in Baden are near Pforzheim and Schwarzwald. The principal Bavarian mines extend about 12 miles from Schwarzenfeld to Nabburg, but the Stulln-Nabburg-Woelsendorf area supplies the greater part of the output. The West German fluorspar mines are well developed and are served by modern milling plants, but reserves are being depleted.

Fluorspar occurs in the Italian Provinces of Lombardy, Trento, and Venetia, and on the Island of Sardinia.

TABLE 1.—*Principal producers of finished and crude fluorspar in the United States in 1963*

Producer	Location of milling plant		Grade
	County	Nearest town	
Colorado:			
Allied Chemical Corp., General Chemical Division	Boulder	Boulder	Acid.
Illinois:			
Aluminum Co. of America	Hardin	Rosiclare	Do.
Hastie & Austin	do	Elizabethtown	Crude.
Goose Creek Fluorspar Mining Co., Inc	do	do	Do.
Hoeb Mining Co., Inc	do	do	Do.
James W. Patton & Sons	do	do	Do.
Minerva Co	do	Cave in Rock	Acid, ceramic, metallurgical.
Do	do	Elizabethtown	Do.
Ozark-Mahoning Co	do	Rosiclare	Acid, ceramic.
Shawnee Mining Co	do	do	Crude.
Tamora Mining Co	do	do	Acid, ceramic, metallurgical.
Ted Joiner	do	Elizabethtown	Crude.
Kentucky:			
Calvert City Chemical Co	Livingston	Dyers Hill	Acid.
C. & L. Fluorspar Co	Crittenden	Marion	Crude.
Craighead & Coats	do	do	Do.
James Green	Caldwell	Princeton	Do.
Kentucky Fluorspar Co. (Broker)	Crittenden	Marion	Ceramic.
Mafluor Corp	do	do	Metallurgical.
Nancy Hanks Mines, Inc	Livingston	do	Crude.
Montana:			
Roberts Mining Co	Ravalli	Darby	Metallurgical.
Nevada:			
J. Irving Crowell, Jr	Nye	Beatty	Do.
Monolith Portland Cement Co	do	do	Do.
Utah:			
Chesley & Black	Juab	Delta	Do.
Willden Bros	do	do	Do.

In Spain the principal mines are in the Provinces of Barcelona, Cordoba, Gerona, and Oviedo. The Caravia and Collada mines in the Province of Oviedo and the Osor mine in the Province of Gerona are the largest producers.

The entire world supply of crude natural cryolite comes from Ivigtut, Greenland. The Danish State owns the deposit, and the Kryolitselskabet Oresund Ald, Copenhagen, has the mining concession. There is no reserve of cryolite in the United States; however, in 1963 synthetic cryolite was produced by Kaiser Aluminum & Chemical Corp. at Chalmette, La., and Ravenswood, W. Va.; and by Reynolds Metals Co. at Bauxite, Ark. In the same year cryolite was reclaimed from pot linings by Aluminum Co. of America at Point Pleasant, Tex.; by Kaiser Aluminum & Chemical Corp. at Chalmette, La., Spokane, Wash., and Ravenswood, W. Va.; and by Reynolds Metals Co. at Listerhill, Ala., and Longview, Wash.

Fluorspar was used in 37 of the 50 States in 1963. The consumption pattern is shifting. Five years earlier 36 percent of the fluorspar was consumed in Illinois, Ohio, and Pennsylvania. These same States used 24 percent of the fluorspar in 1963.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Fluorspar commonly is marketed in three grades—metallurgical, ceramic, and acid. Acid grade contains the highest percentage of CaF_2, metallurgical grade is the lowest, and ceramic grade is considered to be in between.

Metallurgical-grade may be sold in the form of gravel, lump, artificial pellets, or fine flotation concentrate. The lowest acceptable metallurgical grade normally contains at least 60 percent effective calcium fluoride. The usual standard on which prices are published contains 72.5 percent effective CaF_2. The effective value is determined by subtracting from the contained CaF_2 2.5 percent for every percent of silicon dioxide (SiO_2) present in the complete analysis.

Ceramic-grade fluorspar specifications differ substantially according to the requirements of individual buyers. It usually is finely ground and the CaF_2 content ranges from 85 to 97 percent with the bulk of the remainder being SiO_2 and calcium carbonate ($CaCO_3$). A limit usually is placed on iron oxide (Fe_2O_3).

Acid-grade fluorspar should contain a minimum of 97 percent CaF_2, and some specifications contain limitations on SiO_2, $CaCO_3$, and sulfide sulfur.

Chemical and physical requirements of acid-grade fluorspar were set forth in National Stockpile Material Purchase Specifications P–69a, dated February 13, 1952, by Defense Materials Service (DMS), General Services Administration (GSA).

National Stockpile Purchase Specification P–69b–R dated December 2, 1963, contained requirements for metallurgical-grade fluorspar acquired by DMS for the stockpile.

TECHNOLOGY

Geology

In the Illinois-Kentucky district the country rock is limestone, shale, and sandstone. Fluorspar occurs as veins along faults ranging in thickness from a mere film to a width of more than 30 feet and in extensive flat-lying replacement-type deposits in limestone. Residual deposits resulting from weathering of fluorite-bearing veins also are fairly common in the district and often indicate the presence of vein deposits at greater depth (*8*, *15*, *32–33*).[2]

In the Western States fluorspar occurs under a wide variety of conditions—as fillings in fractures and shear zones forming more or less well-defined veins and as replacements in the country rock. Much occurs in igneous formations (*7*, *13–14*, *24*, *28*, *30*).

At Ivigtut, Greenland, the cryolite is associated with pegmatite within an intrusive mass of porphyritic granite. Associated minerals are silica, fluorspar, galena, pyrite, and siderite.

Mining

Fluorspar mining is, in many respects, similar to the mining of metalliferous deposits in steeply dipping veins or in flat-lying deposits. Mining is done by shafts, drifts, and opencuts.

Shaft mines differ greatly in size, capacity, methods of working, and efficiency. At prospect shafts not over 50 feet deep, the simplest mining method may be employed with little other hoisting equipment than a hand-operated windlass and a bucket. At small mines more than 50 feet deep, single-compartment shafts with wood headframes are used; the ore is loaded at the face and trammed by hand on narrow-gage tracks to the shaft, through which it is hoisted by single-drum hoists powered by gasoline engines.

At larger mines the main shafts usually include two hoisting compartments and a manway compartment containing a ladder, air and water pipes, and electric-power conduits. Steel headframes generally have been adopted, and hoisting is done with double-drum hoists with

[2] Italicized numbers in parentheses refer to the items in the list of references at the end of this chapter.

skips or cages. Mining methods follow the practice of metal mines, adopting the method best suited to conditions. Top slicing, cut-and-fill, and shrinkage and open stoping are among the methods commonly used. Bedded deposits are usually worked by a room-and-pillar system. Some of the larger mines are extensively mechanized, using diesel-powered hauling and loading equipment (*1–2, 21–22, 25–26*).

At many fluorspar mines, water pumping is a major element in the mining operation. Large quantities of water enter the mines in the Illinois-Kentucky district through channels in the limestone and from the Ohio River. At the Rosiclare mine, for example, underground water flowed into it at a rate of 7,000 gallons per minute. The Crystal mine in the Cave in Rock area in Illinois has a water problem. When the "Big Sink," a landlocked area covering about 800 acres, rises to a high level because of excessive rains, water seeps into the mine from innumerable underground crevices and fissures and causes it to flood.

Milling

Although some domestic fluorspar is sold with little or no processing after mining, most crude ore requires beneficiation to yield a finished product. Milling practices range from rather simple methods, such as hand sorting, washing, screening, and gravity separation by jigs and tables, to sink-float and froth-flotation processes. Most of the domestic output is produced by sink-float, froth flotation, or a combination. These processes permit utilization of lower grade ore; recovery is much more efficient; and the finished product is of higher quality. Also, the flotation process permits recovery of the lead and zinc minerals often associated with the fluorspar ores (*1, 12, 25, 32*).

To a large extent the selection of a milling process depends on the character of ore to be treated and the type of product desired. Some highly disseminated ores can be treated successfully only by flotation, since fine grinding is necessary to liberate the component particles. Flotation also is commonly used where a pure product of fine particle size is desired, such as ceramic- and acid-grade fluorspar (*23, 34*). The heavy-medium or sink-float process is usually employed where a coarse product, such as metallurgical-grade gravel, is desired, and enough concentration can be achieved without fine grinding (*20*). Some producers use both processes in combination, producing gravel products by sink-float and treating undersize from the heavy-medium mill by flotation; or alternatively, sink-float is used to produce a preconcentrate, which is then used as feed for the flotation plant (*10–11*). There are now seven plants in the United States with facilities for making bricks, briquettes, or agglomerated products from fluorspar fines.

Flotation and other mineral-dressing techniques are employed to treat cryolite.

Chemical processes may be used to recover fluorine from phosphate rock. At present the greater part recovered is in the acidulation step in producing ordinary superphosphate. The fluosilicic acid is sold or used to prepare salts such as ammonium, magnesium, and zinc fluosilicates and sodium silicofluoride. A small tonnage of fluorine in the form of synthetic fluorspar was recovered by the Tennessee Valley Authority (TVA) from stack gases evolved in processing phosphate rock. The recovery process consists of absorbing the fluorine, which is present as hydrogen fluoride, in a bed of lump limestone at temperatures above the dew point of the stack gases. The calcium fluoride reaction product separates from the limestone lumps in the form of fines; portions of the bed are withdrawn from the tower at intervals and screened to remove the fines, and the oversize (partly reacted limestone) is recycled to the tower with fresh limestone (*16, 17, 19*). Because of the cost of purifying fluorine compounds recovered in processing phosphate rock most of the fluorine is neutralized and discarded.

USES

Fluorine is used principally in the form of fluorspar, cryolite, hydrofluoric acid, and fluosilicates.

Until recently the largest use of fluorspar has been as a flux in the manufacture of basic open-hearth, basic electric furnace, Bessemer converters, and basic oxygen steel furnaces. Many other metallurgical operations including the production of iron castings, ferroalloys, and nickel and its alloys; the melting and casting of aluminum and magnesium; the smelting of secondary metals; and the manufacture of fluxing compounds utilize small tonnages of fluorspar. Metallurgical operations consume fluorspar in gravel form, and flotation concentrate has been utilized to a limited degree. The use of pelletized flotation concentrate has not attained wide acceptance in the metallurgical industries, but is now receiving a great deal of attention for use in basic oxygen steel furnaces.

In recent years the greatest use has been in the production of hydrofluoric acid, an essential raw material in manufacturing synthetic cryolite and aluminum fluoride for the aluminum industry, and in many other applications in the chemical industry particularly in the

production of fluorcarbons for aerosols, plastics, and refrigerants. Acid-grade spar requirements of the aluminum industry have expanded rapidly in recent years and parallel the expansion in aluminum production. Cryolite, which serves as an electrolyte in the electrolytic reduction of alumina, is required in large quantities to fill reduction cells when new aluminum-production units are started; and in regular reduction operations cryolite consumed must be replaced by additional cryolite or aluminum fluoride. Based on 1951 data, it was estimated that 47 pounds of cryolite and 58 pounds of aluminum fluoride were consumed per ton of virgin aluminum produced (*3*, p. 7). The largest use of cryolite is in the production of aluminum. The quantity of fluorspar needed to produce a unit quantity of aluminum is being decreased because of increased reclamation of cryolite from pot linings. Smaller quantities are used in abrasives, insecticides, glass, and enamel.

Hydrofluoric acid is used by industry as a source of fluorine to produce refrigerants, propellants, fluorocarbon plastics, and other fluorine compounds; as a catalyst in the production of high-octane aviation fuels; in etching and polishing glass, pickling steel, cleaning metal castings, and enamel stripping; as a laboratory reagent; and for many other industrial uses. An important use for hydrofluoric acid is in the field of atomic energy to produce uranium tetrafluoride from uranium oxide. The tetrafluoride is used in preparing uranium hexafluoride. The most volatile compound of uranium, uranium hexafluoride, has been extensively utilized in the separation of uranium isotopes by thermal diffusion.

The third major use of fluorspar is for ceramic purposes in the manufacture of opal and flint container glass and as an ingredient in enamels for coating steel and cast iron. Ceramic-grade material also is consumed for welding-rod coatings, fiber-glass production, and as an additive to brick clays.

Small quantities of ceramic- or acid-grade fluorspar also are consumed by the magnesium industry.

Small quantities of clean, virtually colorless, and flawless crystalline fluorite have been used in lenses or prisms of microscopes, telescopes, and spectroscopes, but synthetically grown crystals have largely displaced fluorite in these uses.

Markets for the fluosilicates are relatively limited. Fluosilicic acid is used as a disinfectant in the brewing industry, as a preservative, in electroplating, as a concrete hardner, and in the manufacture of silicofluoride salts. Sodium silicofluoride is used for fluorination of community water supplies. In 1963 more than 43 million people in 2,300 towns used fluoride-treated water. Sodium silicofluoride and ammonium fluosilicate are used in insecticides, laundry applications, fluxing, ceramics, and casting light metals. The magnesium and zinc fluosilicates are used as concrete hardeners, and the magnesium salt also finds application in magnesium foundries.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Lead, zinc, and minor quantities of other metals, such as silver, cadmium, and germanium, are often recovered as byproducts or coproducts of fluorspar. The value of lead and zinc produced in the Illinois-Kentucky area in recent years has been substantial. These byproducts are important factors in the economy of many fluorspar operations.

ALTERNATE MATERIALS

No suitable materials to replace metallurgical-grade fluorspar are available. However, blended fluxes using fluorspar as a base are used at some foundries.

The sulfuric acid process for producing high-octane components for gasoline can be used in place of the hydrofluoric acid process; however, the equipment for one acid process does not readily lend itself to the use of the other acid.

There is no satisfactory substitute for fluorspar in the manufacture of hydrofluoric acid.

Owing to its limited occurrence, much of the cryolite consumed in the United States is in the form of synthetic cryolite usually made by reacting sodium aluminate with hydrogen fluoride obtained from acid-grade fluorspar (*27*).

SECONDARY SOURCES AND RECOVERY

At some aluminum plants fluorine compounds are recovered and reused in the aluminum-reduction process.

RESERVES

Fluorspar reserves in the United States were recently estimated by the Federal Geological Survey to total 22.6 million short tons containing 35 percent or more CaF_2 or the equivalent value in combined fluorspar and metallic sulfides (*9*). An additional 12 million tons of lower grade material containing 15 to 35 percent CaF_2 was estimated. The reserve is larger than had been previously estimated by the Geo-

logical Survey because of better reserve information and because it includes substantial quantities of ore found in the last few years. The reserves of Newfoundland have been estimated (*15*) and some information on those containing more than 35 percent CaF_2 in Western Europe, and in the U.S.S.R. and its satellites, was given (*18*). The reserves and grade of fluorspar deposits in Mexico were reviewed in 1960 (*31*).

Information on grades and deposits has been compiled from the Federal Geological Survey, from Hose, from Chermette (*4, 5*), from other sources, and from recent unpublished data on deposits in France. The quantity of ore mined since the last estimate, was deducted from this composite information, and the new estimate of reserves and probable grade is as follows:

	Quantity (million short tons)	*Probable grade or range (percent CaF_2)*
Country:		
United States	18.2	40
Canada	5.0	70–75
Mexico	19.3	65
France	5.0	60–95
Italy	3.1	25–78
Spain	6.5	60–90
United Kingdom	1.7	46–96
West Germany	4.3	35
North Africa	3.3	30–40
South Africa	3.3	[1]
Sino-Soviet bloc	13.2	[1]
Others	4.4	[1]
Total	87.3	

[1] Data not available.

The United States has an enormous reserve of phosphate rock and some authorities have estimated its fluorine content to be equivalent to about 900 million tons of fluorspar. However, recovery of any substantial quantity of this fluorine depends upon the quantity of phosphate rock mined and sold, upon the treatment processes to which the phosphate rock is subjected, and upon further development of economic methods of recovering the fluorine in the desired commercial forms.

No estimate of the cryolite reserve in Greenland is available, but recent reports indicate that exploration has failed to develop appreciable new reserves, and the deposit may be approaching depletion.

SOURCES OF STATISTICAL INFORMATION

Annual and quarterly data on production and shipments of fluorspar are obtained from domestic producers by the Bureau of Mines. Over 95 percent of the consumers of all grades of fluorspar are canvassed quarterly. A biennial consumer canvass covers virtually all of the known consumption. All known importers of fluorspar are canvassed annually for imports and sales by quantity and use. World production and trade data are compiled by the Bureau from numerous sources. U.S. exports and imports are obtained from the U.S. Department of Commerce.

PRODUCTION, CONSUMPTION, AND TRADE

The growth of the fluorspar industry in the United States during the present century has been rapid, particularly since 1941. Annual production increased from an annual average of about 40,000 short tons in the decade 1900–9, to an average of about 323,000 tons during the decade 1940–49. During the same period, average annual imports increased from about 15,000 tons to 57,000 tons. From 1950 to 1963 domestic shipments of finished fluorspar fluctuated from 347,000 tons in 1951 to a low of 185,000 tons in 1959. During the same period there was a tremendous increase in imports of fluorspar from abundant sources in Mexico.

Domestic fluorspar production in 1963 (shipments from mines and mills) totaled 200,000 short tons. As a whole domestic fluorspar has been supplying a declining fraction of the market in recent years. Difficulty in meeting specifications required by buyers and the competition of foreign fluorspar are among the factors which have influenced trends in the industry. Shipments by States with maximum shipments in any year and cumulative shipments to the end of 1963 are shown in table 2, and consumption by States in 1963 is shown in table 3.

Because of lower production costs, and the availability of high-grade ore particularly in Mexico, consumers have generally found the use of foreign ore to be less costly than that from domestic mines.

Imports of fluorspar for several years were greatly stimulated by the strong demands of the consuming industries and the requirements of the national stockpile. Recently, industrial needs have been sufficient to require continued imports of large quantities. In 1963, imports totaled 555,000 short tons valued at $14.1 million, whereas 631,400 tons entered in 1957, 181,300 tons in 1951, and 2,100 in 1942. Mexico has recently been the principal source with several European countries shipping substantial tonnages.

Since 1952, imports have exceeded domestic production and in 1957 a record high of 631,367 short tons was recorded. Mexico has supplied the major quantity of the total fluorspar imported in recent years. In 1963, 80 percent of the imports of fluorspar were from

TABLE 2.—*Shipments of domestic fluorspar by State of origin with shipments of maximum year and cumulative shipments from earliest record to end of 1963*

[Short tons unless otherwise specified]

State	Maximum shipments		Shipments by years							Total shipments to date	
	Year	Quantity	1954–58 (average)	1959	1960	1961	1962	1963		Quantity	Percent of total
								Quantity	Percent of total		
Illinois	1951	204,328	154,889	112,469	134,529	116,908	132,830	132,060	66.1	6,103,345	53.8
Kentucky	1941	141,862	21,217	18,579	25,855	38,898	33,830	35,072	17.6	3,016,980	26.6
Utah	1950	18,936	9,902	(2)	1,912	610	399	247	.1		
Montana	1957	64,339	43,619	18,542	31,273	14,905					
Nevada	1953	(1)		16,743	18,505	18,129					
Arizona	1953	1,951		2 18,558			38,967	32,464	16.2		
California	1934	181	71,028	(2)						2,211,608	19.4
Colorado	1944	65,209		(2)	17,708	15,633					
New Mexico	1944	42,973		200							
Tennessee	1956	(1)									
Idaho	1952	(1)									
Other States 3	(3)	(3)								23,482	.2
Total	1944	413,781	300,655	185,091	229,782	205,083	206,026	199,843	100.0	11,355,415	100.0

1 Figures withheld to avoid disclosing individual company confidential data, included with total.

2 Shipments from Arizona, California, Colorado, and Utah are combined to avoid disclosing individual company confidential data.

3 Comprises New Hampshire, 1917, 1,274 tons, total shipments 8,302 tons; Texas, 1944, 4,769 tons, 1949–53 (average) 498, total shipments, 14,779 tons; Washington, 1945, 132 tons, total shipments 382 tons; and Wyoming, 1944, 19 tons, total shipments 19 tons: Total shipments 23,482 tons.

TABLE 3.—*Fluorspar (domestic and foreign) consumed in the United States, by States in 1963*

[Short tons]

State	Quantity	State	Quantity
Alabama, Georgia, North Carolina, South Carolina	11,604	braska, South Dakota, Wisconsin	3,857
Arkansas, Kansas, Louisiana, Mississippi, Oklahoma	84,592	Kentucky	41,183
California and Hawaii	30,195	Maryland	8,257
Colorado and Utah	21,221	Massachusetts	163
Connecticut	1,414	Michigan	40,328
Delaware and New Jersey	133,695	Missouri	2,313
Florida, Rhode Island, Virginia	1,131	New York	14,114
Illinois	47,597	Ohio	65,198
Indiana	27,573	Oregon and Washington	1,477
Iowa, Minnesota, Ne-		Pennsylvania	64,898
		Tennessee	2,600
		Texas	89,529
		West Virginia	43,411
		Total	736,350

Mexico. Italy and Spain have supplied all but a small part of the remainder. European fluorspar generally enters at Philadelphia; Canadian at Buffalo, Cleveland, New York, and Philadelphia; and the Mexican at Douglas, Ariz., and Brownsville, Eagle Pass, El Paso, and Marathon, Tex. Imports are shown in table 4.

Tariff rates in effect in December 1963 on fluorspar containing more than 97 percent CaF_2 was $1.875 per short ton ($2.10 per long ton) and less than 97 percent CaF_2 was $7.50 per short ton ($8.40 per long ton).

There is no tariff on cryolite.

During the 2½ years Public Law 733 was in existence, the domestic producers had shipped 156,603 short tons valued at $8,477,202 to the supplemental stockpile.

Increased consumption of fluorspar in the United States has been principally a result of growth in the requirements of the steel and aluminum industries, and increased use of fluorine chemicals. Consumption statistics by uses are shown in table 5.

TABLE 4.—*Fluorspar imports by countries of origin*

[Short tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963
Canada	27,344	11,440	8,183	2,351		73
Germany, West	23,073		13,711	7,115	3,472	399
Italy	69,603	135,231	96,124	62,310	47,803	33,074
Mexico	256,756	327,045	287,528	344,141	447,364	443,534
Spain	54,524	71,616	108,632	87,994	82,869	68,323
Other countries	1,865	10,418	19,842	1,848	14,187	9,720
Total	433,165	555,750	534,020	505,759	595,695	555,123

TABLE 5.—*Fluorspar consumed in the United States by uses*

[Short tons]

Use	1954–58 (average)	1959	1960 1	1961	1962	1963
Hydrofluoric acid	270,089	324,519	372,654	418,612	366,298	414,500
Glass	31,018	30,175	26,957	27,696	28,875	31,465
Enamel	5,481	5,751	4,815	4,761	5,169	5,516
Steel	225,871	194,230	214,563	204,842	214,439	242,824
Iron foundry	13,269	13,529	11,810	10,053	13,454	17,125
Ferroalloys	3,161	3,381	2,543	2,401	2,172	2,010
All other	13,292	18,394	10,417	19,575	22,481	22,910
Total	562,181	589,979	643,759	687,940	652,888	736,350

1 Glass, enamel, and other (including welding rod coatings, nonferrous, special flux, and ferroalloys), partly estimated from sample canvass of consumers who accounted for more than 95 percent of total usage in 1959.

According to latest export statistics about 42 percent of the fluorspar produced throughout the world in 1963 entered foreign trade (see table 6).

STRATEGIC CONSIDERATIONS

Until recent years the United States, the largest consumer of fluorspar, had been able to provide the bulk of its needs from domestic mines and mills; however, recently the consuming industry has expanded at a rapid rate and imports in 1963 provided about three-fourths of the total fluorspar consumed. The proportion provided by imports is expected to increase. As consumption is expanding more rapidly than domestic production the United States has become less self-sufficient in fluorspar supplied, although ample reserves are available for development.

The strategic stockpiles are intended to supplement domestic production in time of emergency, when some foreign sources would not be available to this country. Ample stocks of acid-grade fluorspar were readily accumulated, but difficulty was encountered in building up metallurgical stocks. On June 30, 1964, Government inventories of acid-grade fluorspar totaled 1,144,100 tons, of which 458,100 tons was in the national (strategic) stockpile, 17,300 in DPA stocks, and 668,700 in the supplemental stockpile. Stocks of metallurgical-grade totaled 412,200 tons, of which 369,400 was in the national (strategic) stockpile, and 42,800 in the supplemental stockpile.

GOVERNMENT PROGRAMS

Under authority contained in Public Law 701 of 1958, the Office of Minerals Exploration was created on July 1, 1958, to provide Federal financial participation in the exploration for new mineral reserves. The Government will contribute 50 percent of the total allowable cost of the exploration work specified by the terms of the contract.

PRICES AND COSTS

Market price quotations on domestic and foreign fluorspar are regularly published in E&MJ Metal and Mineral Markets and in Steel magazine and quarterly in the Chemical and Engineering News magazine. In the Oil, Paint and Drug Reporter, prices that indicate

TABLE 6.—*Production and trade of fluorspar in 1962, by major countries*

[Short tons]

Exports, by countries of origin	Production	Exports	Exports by countries of destination								
			North America		South America	Europe		Asia		Africa	Australia
			Canada	United States		East	West	Japan	Other		
North America:											
Canada	[1] 75,000	4					4				
Mexico	553,642	516,216	[2] 52,905	[2] 447,365	77		12,453	[2] 1,270	[2] 2,146		
United States	[2] 206,026	1,308	1,144		112		1	6	45		
South America: Argentina	9,976	637			637						
Europe:											
Bulgaria	([4])	[5] 2,342					[2] 1,306	[2] 1,036			
France	237,200	48,688		3,585			44,560			543	
Germany:											
East	[1] 80,000	[3] 4,652					[2] 4,652				
West	[6] 116,592	15,802		3,781	64		11,957				
Italy	171,474	54,142		51,095			[2] 2,456		591		
Spain	[6] 165,356	97,004		82,802			13,938		264		
Sweden	[7] 3,900	531					508		23		
United Kingdom	79,525	([5])									
Asia:											
China	[1] 220,000	[2] 119,009				[2] 62,832	[2] 22,302	[2] 29,231	[2] 4,644		
Japan	17,120	64							64		
Korea:											
North	[1] 33,000	[3] 4,525						[3] 4,525			
Republic of	36,343	26,027					166	24,641	1,220		
Mongolia, Outer	[1] 44,000	[2] 41,337				[2] 41,337					
Thailand	11,806	7,674						6,462	1,212		
Turkey	640	([5])									
U.S.S.R.	[1] [8] 230,000	5,512						5,512			
Africa:											
South Africa, Republic of	111,683	78,187	10,915		242	1,058	21,863	[2] 34,384	142	7,021	2,562
South-West Africa	240	115		1				1		113	
Other Africa	566										
Total	[4] [9] 2,410,000	1,023,776	64,964	588,629	1,132	105,227	136,166	107,068	10,351	7,677	2,562

[1] Estimate.
[2] Imports.
[3] Shipments.
[4] Fluorspar is also produced in Bulgaria, data not available; estimate included in total.
[5] Incomplete data.
[6] Marketable.
[7] Sales.
[8] U.S.S.R. in Europe included with U.S.S.R. in Asia, as the deposits are predominantly in Asiatic U.S.S.R.
[9] Data do not add exactly to totals shown because of rounding where estimated figures are included in the detail.

the high and low offerings on cryolite and other fluorine compounds are quoted. Actual prices are negotiated between the buyers and sellers on the basis of specifications.

Table 7 shows the average value to specified industries. The average value of all grades of domestic fluorspar shipped reached a record high in 1954, and prices have fluctuated since that time.

TABLE 7.—*Average value of domestic fluorspar shipped to specified industries, per short ton*

Use	1954–58 (average)	1959	1960	1961	1962	1963
Hydrofluoric acid [1]	$56.23	$54.25	$52.80	$52.10	$49.61	$51.99
Glass	42.15	42.73	43.56	43.38	42.08	42.16
Enamel	46.00	45.57	46.07	45.74	43.02	41.59
Ferrous [1]	[2] 30.71	31.45	30.02	29.21	32.15	34.26
All industries (includes exports)	46.73	46.90	45.22	45.30	44.49	45.03

[1] Shipments to the General Services Administration included under hydrofluoric acid for 1954–58 and steel (ferrous) for 1956–58.
[2] Includes iron foundry for 1955.

TAXES

Producers are granted a depletion allowance of 23 percent on domestic production and 15 percent on foreign production. Under the Defense Production Act the Accelerated Tax Amortization grants totaled $4,282,000. This program closed December 31, 1955.

TRANSPORTATION

Fluorspar is shipped by a variety of methods. Crude fluorspar may be hauled from the mines by truck to the mill or processing plant, and in this crude state it may be shipped by rail in open gondolas or hopper cars directly to the consuming industry. Finished fluorspar in the form of flotation concentrates may be shipped to consumers in 100-pound bags (four bags to a barrel) in boxcars, or in bulk in covered hopper cars. In the Illinois-Kentucky district several producers maintain loading facilities on the Ohio River for barge shipment to the Pittsburgh, Pa., area.

Handling and haulage techniques developed originally for shipping rocket fuels by trucks now enable chemical manufacturers in any part of the country to order liquid fluorine by the ton (*6*). One chemical manufacturer worked several years to develop a tank system having no moving parts or mechanical refrigeration. Having a fluorine capacity of 2½ tons, the system weighs 10 tons and consists of three horizontal cylindrical tanks one inside the other mounted on a semitrailer. As fluorine's normal boiling point is −306° F, the innermost tank containing the liquid fluorine is surrounded by a tank of liquid nitrogen (−320° F) and an outer tank filled with perlite or Santocel insulation and is then evacuated. Evaporation of the fluorine is prevented by the liquid nitrogen while nitrogen losses are effectively minimized by the efficient outer insulation.

RESEARCH

Fluorspar research in industry usually is directed toward improving mining and milling processes, changing the properties of finished concentrates, reducing the cost of these processes, and conducting reserve studies.

The Bureau of Mines has engaged in several projects involving research on the recovery of fluorspar and other fluorine compounds from phosphate rock and low-grade or complex fluorspar ores. Occasionally, fluorspar deposits are examined and studies made of mining methods and costs. Fundamental data on fluorine compounds are accumulated and published as a part of the Bureau's research on the thermodynamic properties of mineral materials.

OUTLOOK

Both the short- and long-term supply outlook for all grades of fluorspar required by domestic consumers are favorable, based on reserves in North America. Domestic production will probably continue to supply only about 20 to 35 percent of domestic consumption. Relatively low-cost and high-grade imported fluorspar will continue to restrict the movement of the domestic product, and the low prices of imported fluorspar will discourage expansion of the domestic industry.

Fluorine consumption is expected to increase as it has almost without interruption since the end of World War II. The growing aluminum, steel, and chemical industries will require more fluorine compounds. At the same time, it is likely that more cryolite will be reclaimed and reused at aluminum plants. Probably the greatest potentials for expansion lies in the relatively new and rapidly growing field of fluorine chemicals. The increasing use of the basic oxygen process in steelmaking expands the fluorspar market because this process requires about five times as much fluorspar per ton of steel as the basic open-hearth process. Fluorocarbon compounds, used for refrigerants, propellants, fluorinated plastics, and other fluorine compounds, can be expected to be used in increasing quanti-

ties in many applications. Fluorine is the active object of a wide variety of research in both organic and inorganic chemistry, and new uses are being discovered and developed.

The long-range trend in domestic fluorspar production is contingent upon the degree of competition from comparatively low-priced imported fluorspar, the price structure, and changes in tariff regulation, import restrictions, or market control. Production would also be affected by the solution of several technical problems involving the development of additional uses, reduced cost of distribution, and increased efficiency in exploration, development, mining, and milling.

In processing phosphate rock to make superphosphate fertilizers, gases are evolved which contain fluorine. Although plants in three States are now making or are capable of making synthetic cryolite from fluorine in processing phosphate rock, synthetic cryolite from this source is not expected to become a major factor in the fluorine market until far in the future when the price of fluorspar increases substantially. The development of an efficient, low-cost process for converting the silicofluoride to aluminum fluoride, synthetic cryolite, or other compounds suitable for industrial uses would change this outlook and increase the relative value of this source of fluorine. At present most phosphate producers find it more economic to neutralize the fluorine gases and discard the product than to recover the fluorine and attempt to sell it in a limited market.

The only free world source of natural cryolite is at Ivigtut, Greenland. This property has been operated for many years and its exhaustion is now within sight. Natural cryolite is comparatively expensive, so a synthetic cryolite industry has come into existence which uses fluorspar as a source of fluorine. The manufacture of cryolite from aluminum fluoride in the potline at aluminum plants, and additional reclaimed cryolite are expected to decrease the need for making this material separately from fluorspar.

PROBLEMS

The immediate problem of the domestic fluorspar-producing industry is to regain a portion of the domestic market that has been lost to imported material.

Defining the true strategic position of fluorspar also is a problem. Acid-grade and metallurgical-grade fluorspar are defined as strategic materials. Curtailment of domestic production has changed the Nation's supply picture and has provoked argument. One faction argues that domestic production should be maintained at all costs to keep mines in operation for an emergency, but the other attitude is that available nearby supplies (Mexico and Canada) are practically equivalent to a domestic supply.

Operators are often faced with the problem of whether to continue operating at a loss and maintaining resources or closing and running the risk of losing the mines. Although sizable resources are known, most domestic fluorspar deposits are underground, lower grade, and less accessible than many of the high-grade surface deposits in foreign areas which contribute major tonnages to the domestic market. In addition, a substantial tonnage of resources has been lost by flooding and caving-in of mines forced to shut down because of economic conditions. Other resources have been lost by the selective mining of high-grade areas.

A continuing long-term problem of the domestic fluorspar industry is the maintenance of a satisfactory reserve position.

The domestic fluorspar output is hampered by comparatively high costs of exploration, development, mining, beneficiation, and transportation. Production at some mines is hampered by excessive water.

Complexity of some of the domestic ores, stringent specifications on contaminants, and difficulties encountered in the utilization of low-grade ores are all major fluorspar problems.

Maintenance, classification, and interpretation of available statistical data for the guidance of Government and industry is a growing problem as the economic conditions change and complexities of fluorine production and consumption increase. Data are lacking from several areas of the statistical pattern, including recovery of fluorine from phosphate rock and secondary recovery as cryolite.

A quicker, more accurate field method of analyzing complex ores for fluorine is required, as present methods are slow, cumbersome, time consuming, and relatively expensive.

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GALLIUM

By Donald E. Eilertsen [1]

GALLIUM, discovered in 1875, was not produced commercially in the United States until 1943. The element is notable because it melts at 30° C, or about 86° F. The metal is recovered commercially as a byproduct in the extraction of alumina from bauxite and zinc from sphalerite; production is small. Gallium's largest use and largest interest in research in recent years have been as a semiconductor. Other uses are in selenium rectifiers, in dental alloys, and as a sealant for glass joints in laboratory equipment. The resource of gallium in bauxite and zinc reserves is very large.

BACKGROUND

Gallium was discovered in 1875 and first produced in the United States in 1915 from metallic residues obtained in redistillation of zinc spelter during the extraction of zinc from zinc mineral concentrate. Several thousand grams of gallium were produced commercially from domestic ores during 1943–45; production was almost 200 pounds in 1948. Three firms produced gallium for a number of years, but in recent years there have been only two.

ORGANIZATION AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

The Aluminum Company of America, Bauxite, Ark., produces gallium metal, and The Eagle-Picher Co., at its Miami plant near Quapaw, Okla., produces gallium metal and compounds. Gallium is a minor byproduct at both companies mineral processing plants.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Gallium (Ga), silvery white in high-purity form, has atomic number, 31; atomic weight, 69.72; melting point, 29.78° C; boiling point, 2,403° C; and densities as follows: 5.904 grams per cubic centimeter (g/cm^3) at 29.6° C (solid), 6.095 g/cm^3 at 29.8° C (liquid), and 5.445 g/cm^3 at 1,100° C. Some of its other properties follows: Expansion upon solidifying, 3.2 percent; specific heat from 12.5° C to 200° C, 0.095 calorie per gram per degree centrigrade; and latent heat of fusion, 19.16 calories per gram (*1*).[2] Liquid gallium aggressively attacks solid metals, especially at high temperatures, and is extremely difficult to contain. Gallium and its compounds are generally nontoxic.

Gallium purities are sometimes expressed in terms of nines; that is, 99.999 percent pure gallium is 5–9s purity.

Gallium metal and some of its compounds are available in very high purities such as 99.99999 percent purity gallium (7–9s), and 99.9999 purity gallium sesquioxide (6–9s.)

TECHNOLOGY

Mineralogy and Occurrence

The earth's crust is estimated to contain 15 parts per million of gallium, compared to 16 parts per million of lead. Gallite, $CuGaS_2$, from South-West Africa is the only known mineral that contains gallium as an essential constitutent, but the quantity of gallite seems to be small (*3*). Numerous minerals contain gallium as an impurity. Almost all highly aluminous rocks and minerals contain detectable gallium. It has been identified in many minerals; among them are adamite, alunite, amazonite, bauxite, beryl, coal, diaspore, enargite, gahnite, germanite, hopeite, lepidolite, margarite, microcline, muscovite, parahopeite, phlogopite, sphalerite, spodumene, and tennantite. Gallium is recovered commercially as a byproduct in the United States from impure bauxite and impure sphalerite. The gallium content of sphalerite from the Tri-State area

[1] Commodity specialist.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

ranges from 0.001 to 0.02 percent, and averages about 0.005 percent. Bauxites are known to contain up to 0.01 percent gallium.

Germanite, a complex sulfide of copper, iron, and germanium found in East Germany and South-West Africa, has been known to contain up to 1.85 percent gallium.

Metallurgy

In the Bayer process for extraction of alumina (Al_2O_3), bauxite is digested in caustic solution and the major impurities, ferric oxide and silicon dioxide, are separated from the alumina. The alumina subsequently is precipitated and the spent caustic solution containing gallia (Ga_2O_3) is recycled to treat more bauxite. Owing to continuous reuse of the caustic solution, the gallia builds up to an equilibrium concentration and additional gallia then precipitates along with alumina. Gallium is recovered from the caustic solution by chemical and electrolytic procedures (*1*).

In zinc extraction operations, gallium might appear in the following products:

Residues from primary retorts, spelter from primary distillation, residues from redistillation of primary spelter, residues from zinc oxide furnaces and Waelz kilns, purification precipitates of zinc sulfate solutions at electrolytic plants, and residual zinc sulfate solution at lithopone plants.

The Eagle-Picher Co. separated gallium from the iron residue resulting from the production of zinc sulfate solution from sphalerite. Gallium hydroxide is separated from iron hydroxide, is converted to trichloride, and is purified by ether partition. The purified gallium trichloride is converted to sodium gallate and is electrolyzed, using a copper rod cathode and platinum anode. The cell temperature is kept well above 29.75° C, the melting point of gallium. Electrolysis is at 5.5 volts and 0.5 ampere per square centimeter of anode and 0.33 ampere per square centimeter of cathode. Liquid gallium collects on the tip of the cathode and drains into a poreclain crucible.

The crude liquid gallium is washed several times alternately with distilled water, dilute hydrochloric acid, and dilute nitric acid. A dark colored dross formed during the nitric wash is removed by skimming. Chemical cleaning of the gallium is complete when no dross forms during the nitric wash and when the gallium forms a mirror-like pool after the hydrochloric treatment. The liquid metal is cooled below its melting point, is seeded with crystalline gallium, and gallium crystals are removed as they form. They are dried, packed in pliofilm or rubber bags, and kept at about 15° C (*6*).

USES (*1*)

The largest use at present by far for gallium and some of its compounds is in semiconductors and in research and development of electronic devices. The availability of extremely high-purity gallium and some of its compounds has led to the production of semiconductors with properties closely approaching those predicted from theory. Some of the new developments include use of gallium as a dopant for semiconductors, and use of gallium arsenide in high-temperature and high-frequency transistors; tunnel diodes which have applications in switching and FM transmitter circuits, replacement for phase-locked ocillators, and amplifiers; solar cells for solar batteries; and in research concerning use of lasers.

Other applications include the uses of gallium oxide for vapor-doping of other semiconductor material; of the oxide and halides for epitaxial growth of gallium arsenide and gallium phosphide; and of gallium ammonium chloride in plating baths for electrodepositing gallium onto whisker wires for leads of transistors.

Gallium metal is used in certain selenium rectifiers, as sealant for glass joints in mass spectrometers and other laboratory equipment, as backing for mirrors, and for special thermometers.

Gallium has promising application in alloys. For example, a certain dental alloy can support the pressure of a ton on a 0.03-square-inch area, a compressive pressure of 33 tons per square inch. Gold-platinum-indium alloys are being used for dental restorations. Two other dental alloys are being reevaluated, one containing 14 percent gallium and 86 percent of a silver alloy, and the other alloy containing 36 percent gallium, 62.1 percent nickel, and 1.88 percent silicon. Certain vapor-arc lamps contain gallium-cadmium-zinc alloys. Other gallium alloys are used as low-resistance contact electrodes for bonding wire and thermocouples to ferrites and semiconductors.

ALTERNATE AND SUBSTITUTE MATERIALS

Substitutes are known for almost all of gallium's commercial applications but the performance may not be as good as for gallium. In the field of semiconductors germanium, silicon, indium antimonide, and indium arsenide are some of the competitors of gallium arsenide. Although gallium can sometimes be substituted

for other metals, cheaper metals usually are used instead of gallium.

RESERVES

Rough estimates of the gallium resources in bauxite and zinc reserves are obtainable by assuming that the bauxite resource contains 0.004 percent gallium and zinc resources contain 0.006 percent gallium. The resource of gallium from these sources, in short tons, is as follows:

	United States	World
Gallium in bauxite reserves	2,000	230,400
Gallium in zinc reserves	720	5,460
Total	2,720	235,860

SOURCES OF STATISTICAL INFORMATION

Data on domestic production and consumption of gallium are obtained by the Bureau of Mines through industry canvasses; however, company confidential data are not publicized.

Data on imports of gallium metal are obtained by the Bureau of Mines through the U.S. Department of Commerce. No data are available on imports of gallium compounds and exports of gallium metal and its compounds.

PRODUCTION, CONSUMPTION, AND TRADE

Estimates indicate that gallium output could be increased substantially if needed. Aluminum Company of America and The Eagle-Picher Co. have been the only gallium producers in the United States in recent years. In 1946–63, gallium was produced by The Aluminum Company of America during 1947–48, 1950–51, 1953–63; and by The Eagle-Picher Co. during 1946–48, and 1957–63. Record output of domestic gallium occurred in 1961, while record shipment of gallium occurred in 1963.

Gallium is produced in approximately six foreign countries. Figures on imports of gallium have been available since September 1, 1963, when a new system of reporting began. Imports of unwrought gallium and waste and scrap for consumption during September–December 1963 were 1 pound, valued at $486, from France; 16 pounds, valued at $7,000, from Switzerland; and 1 pound valued at $606, from the United Kingdom.

Tentative general imports of these materials during 1964 were 5 pounds, valued at $1,037, from France; 321 pounds, valued at $64,389, from Switzerland; 55 pounds, valued at $9,842, from the United Kingdom; 14 pounds, valued at $3,056, from West Germany; 22 pounds, valued at $4,943, from Hungary; and a quantity to be confirmed, valued at $3,846, from Mexico.

Duty of 50 cents per long ton on bauxite has been suspended. Sphalerite concentrate is dutiable at 0.67 cent per pound of zinc content. Gallium metal is dutiable at 10.5 percent ad valorem.

STRATEGIC CONSIDERATIONS

The United States is self-sufficient in gallium because gallium output could be greatly increased if needed, but perhaps at higher prices. Gallium is not on the Government's list of strategic and critical materials for stockpiling.

PRICES

TABLE 1.—*Market prices of gallium from bauxite sources in 1963–64*

[Per gram]

Quantity	99.99 percent	99.999 percent	99.9999 percent
Up to 999 grams	$1.40	$1.50	$1.70
1,000 to 4,999 grams	1.20	1.30	1.50
5,000 to 24,999 grams	1.10	1.15	1.35
Over 25,000 grams	.95	1.00	1.20

RESEARCH

Gallium semiconductors materials have been the subject of intense research and development in recent years.

The bibliography of gallium is extensive (*2, 4–5*).

Currently, the Bureau of Mines is conducting studies on gallium alloying and extraction of germanium and gallium from coal-fly ashes and flue dusts.

OUTLOOK

Gallium, abundant as lead in in the earth's crust, is found in nature only as a minor constituent in various minerals, the commercial source being certain bauxites and sphalerites. Producers could increase gallium production fourfold or fivefold with equipment now in use, and additional capacity could be built easily if needed.

Consumption seems likely to continue at small quantities annually, the largest use being in intermetallic compounds for semiconductor applications and in research in this field. Conventional uses will continue for gallium in certain selenium rectifiers, as a material for sealing glass joints and valves in laboratory vacuum equipment, for backing mirrors, for special thermometers, and for low-melting alloys used in dentistry. Significantly greater demand for gallium is not likely unless some unexpected research development occurs, such as in extensive semiconductor application. Currently gallium arsenide shows promise for application in high-temperature and high-frequency transistors, lasers, and tunnel diodes.

PROBLEMS

The principal gallium problem is the lack of demand. Despite its unusual properties only a small fraction of the potential output from bauxite and sphalerite sources has been achieved.

Problems associated with gallium extend from detection through refinement and development of uses. Despite the abundance of gallium its occurrence in nature is irregular. The prospector finds it difficult to detect gallium in the field. Source materials are so low in gallium that costly multistage extraction techniques have to be employed to enable good recovery. The resultant high price restricts demand and serves as a barrier in the development of new applications.

There is insufficient knowledge of the physical and chemical properties of gallium metal and its alloys and compounds, to stimulate their application. Gallium's corrosive attack on other metals at elevated temperatures leads to contamination from vessels holding it during alloying, thus adversely influencing the properties of gallium-bearing intermetallic semiconductors produced. Gallium is so reactive chemically at high temperatures that use of the liquid metal in thermal transfer applications such as in nuclear energy would require special metal container materials.

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GARNET

By Paul M. Ambrose [1]

GARNET is a semiprecious gem; however, because of an unusual combination of properties, its main usefulness is as an industrial abrasive. It is used extensively in glass grinding, metal lapping, and wood, leather, and plastic sanding where close quality control is required.

Since 1878 garnet has been used extensively in the United States in manufacturing abrasive papers and cloths. In recent years it has been used as a sandblasting abrasive; for grinding plate glass, optical lenses, and other glass surfaces; and for metal polishing. Eleven abrasive manufacturing companies are producing garnet papers and cloths in the United States.

Peak garnet output in the United States was reached in 1963, when 14,626 short tons was sold. The Barton mine in New York is the largest garnet producer in the world. It has been operated continuously since 1878 and has a large ore reserve. Production from alluvial garnet deposits in Idaho supplies the Pacific Coast States with a sandblasting material. Other garnet output is mainly a byproduct from the milling of other materials.

In 1963 the reported value ranged from $25 per ton for garnet produced in Idaho to $140 per ton for New York garnet.

The currently producing garnet mines are able to satisfy market requirements, and exhaustion of the major sources of supply is not in prospect.

The use of garnet is expected to increase in proportion to the growth of the abrasive industry. The overall problem of the abrasive industry is the lack of definitive criteria for comparing the merits of various abrasive materials. The principal problems of the established producers of garnet are maintaining and increasing sales in the face of active competition from other abrasives.

BACKGROUND

This chapter deals solely with industrial garnet. Gem quality garnet is included in the Gem Stones chapter.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Abrasive garnet production began in the United States in 1878 at the site of the present Barton mine, which since has been owned continuously by the same family. In 1878 less than 100 tons was mined, and this output was used in coated abrasives (papers and cloths). With minor fluctuations, industrial garnet sales increased to a peak of 14,626 tons in 1963. Since 1951 the annual value of sales has averaged more than $1 million.

Barton Mines Corp., the largest domestic producer, operates the Barton open-pit mine and mill near North Creek, Warren County, N.Y. The output is sold directly to consumers, chiefly in the Northeastern States, as graded material. About 60 percent of the output is used to manufacture coated abrasives; the remainder is used for glass grinding and other miscellaneous uses. The Idaho Garnet Abrasive Co., and Emerald Creek Garnet Milling Co., Fernwood, Idaho, mine an alluvial garnet deposit by dragline excavator. The concentrate is sold on the Pacific coast for sandblasting and spark-plug cleaning. Porter Brothers Corp. of Boise, Idaho, recovers garnet as a byproduct from dredging operations in Valley County, Idaho. Small quantities of low-value garnet are produced as a byproduct of wollastonite mining by Cabot Minerals Division, Cabot Corporation, Willsboro, N.Y.

[1] Commodity specialist.

Garnet-coated abrasive papers and cloths are produced by 11 manufacturers at plants distributed as follows: New York, three; Connecticut, Massachusetts, and Michigan, two each; and Minnesota, Ohio, and Tennessee, one each.

Although garnet is found throughout the world and is mined in many countries as a gem material, its production for industrial use is recorded only in the United States, Argentina, Malagasy Republic, Spain, Tanganyika, Republic of South Africa, and the U.S.S.R. The deposits in the U.S.S.R. are similar to the Barton Mines deposit in the United States, and the mill design was based on a former Barton Mines flow sheet.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Garnet is the name of a group of iron-aluminum silicate minerals having similar physical properties and crystal form. Of the many varieties known, almandite ($FeO \cdot Al_2O_3 \cdot SiO_2$) is the most important to industry. Crude garnet ore or concentrate is no longer marketed. Consumers purchase material crushed, ground, and graded to various screen and micron sizes depending upon their needs. The distinctions between grain sizes and powder sizes is arbitrary because there is no exact line which separates grain and powder.

Government specifications for garnet coated abrasives are included in Federal Specifications: P–p–121a June 17, 1953; p–p–00121b (GSA–FSS) interim; and P–P–126a(1), May 16, 1960.

TECHNOLOGY

Almandite, the most important type of garnet industrially, has a hardness of 7.5 to 8, a specific gravity of 4, a melting point of 1,315° C, a color of various shades of red, and a chemical composition of $FeO \cdot Al_2O_3 \cdot SiO_2$; it crystallizes in the cubic system. The sharp fracture and toughness of almandite make it desirable for certain abrasive uses.

At the Barton mine the garnet occurs in a metamorphosed igneous rock, the ore body being 150 to 200 feet wide with outcroppings that can be traced more than 4,000 feet (*6*).[2] The garnet content of the part of the ore body being mined ranges from 12 to 15 percent. Single crystals 1 foot in diameter are common. The garnet has two sets of jointing planes at approximately 90°, which control the shape of the crushed particles. It is believed that the exceptional abrasive quality of garnet from the Barton mine can be attributed to this unusual feature. Garnet in the weathered zone, which extended to a depth of approximately 15 feet, was easily hand-sorted, and it was not until mining of the unweathered rock began that a concentration plant became necessary.

The mine consists of a series of opencut benches. The broken ore is loaded into trucks by power shovels for transportation to the mill, about one-quarter of a mile away.

Separation of the gangue minerals from the garnet is achieved by a combination of methods including jigging, tabling, flotation, magnetic separation, water sedimentation, and air separation.

The first step towards separation begins with crushing followed by a series of grinding steps until each particle of garnet is free of its matrix rock or various minerals which had been intruded or encased in the garnet crystals. Liberation is completed only after garnet particles have been ground to grain and powder sizes that can be marketed. After liberation has been effected in each size range, a close grading is necessary before separation. This sizing is done by screening or water sedimentation. In some cases the same process will perform sizing and separation but in most cases consecutive processes are required. In all cases liberation, separation, and sizing are necessary to obtain marketable garnet.

The distinction between grain sizes and powder sizes is arbitrary because there is no exact line which separate grain from powder. Each results from the same grinding or regrinding which precedes the sequence of separation-grading-separation. Each requires both liberation and separation; the complicating factor is that different size ranges require different types of processes or combinations of processes. Unfortunately no process of grinding can control particle size distribution.

Final grade specifications, some of which are government applied, some industry applied, and some determined by individual customer requirements, are so close and exacting that in any given range of sizes only certain segments of the range can be extracted and made into marketable grades. The in-between sizes which fall outside of the grades at either end must be reground into still finer material. This process is repeated as often as necessary until the particles eventually fall within a grade specification which is marketable. In many cases good milling technique has dictated that final grading be achieved before final separation. Garnet which undergoes regrinding is either garnet which has not been entirely liberated or garnet in "in between" or unmarketable particle sizes. Thus a continuous series of grinding and processing steps are required despite the fact each

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

regrinding as well as the original grinding produces in varying amounts the entire range of grain and powder sizes, some of which are uncontrollably reduced beyond that size for which any market exists.

During the entire milling operation there are two basic objectives; purifying the concentrate and sizing the garnet into marketable grades. Garnet processing includes packing because in this final operation great care and control must be exercised to prevent a mixture of grades or a single particle of contamination from entering the container. A prime objective also is to capture the maximum portion of the garnet in the ore.

The abrasive qualities of garnet are improved considerably by roasting for several hours at 800° to 900° C. This has the effect of increasing its toughness and abrasive properties. Temperatures higher than 1,000° C have a detrimental effect on the final product.

Extensive alluvial deposits of almandite garnet occur on Emerald Creek, Benewah County, Idaho. An overburden of 3 to 8 feet is stripped to expose gravel containing as much as 20 percent garnet. Mining is done with a dragline dredge. The material passes to a trommel and then is treated in jigs and on concentrating tables. The maximum garnet grain size is three-sixteenth inch. The garnet concentrate is dried, crushed, and screened to produce the different sizes required by industry. The crushed material is a better abrasive than the uncrushed because sharper cutting edges are formed.

A garnet concentrate is obtained as a byproduct of wollastonite mining at Willsboro, N.Y. It has been produced as a byproduct of rutile mining near Melbourne, Fla., and from the reworking of mill tailings at Bishop, Calif. Only a limited market has been developed for this byproduct garnet.

USES

The major industrial use for garnet since before 1880 has been as an abrasive material in such applications as optical lens grinding, plate glass grinding, lapping of semiconductor materials and metals where a high quality, scratch-free surface is required. It is also used in nonskid floor paint. Coated papers and cloths are used for finishing wood, leather, hard rubber, felt, and plastics. Spark plug cleaning is a minor use.

The aluminum, aircraft, and shipbuilding industries in California and the Pacific Northwest have found alluvial garnet principally from Idaho to be a good material for sandblasting.

ALTERNATE MATERIALS

Garnet has achieved a unique place in the coated-abrasive field between low-cost quartz and high-cost artificial abrasives (silicon carbide and aluminum oxide). Garnet is preferred over quartz, as it is more efficient and its fracture imparts a more desirable finish to products made of wood, leather, hard rubber, felt, and plastics. Garnet abrasives cannot compete with artificial abrasives for most metalworking applications because of its friable nature and lower hardness rating. If garnet were not available, quartz and artificial abrasives could be used in its place.

RESERVES

New York has the largest known garnet reserve in the United States, the supply being adequate for the foreseeable future. For many years the reserve has been developed through exploration at a rate at least equal to consumption. The quantity of garnet-bearing gravel at Emerald Creek, Idaho, is reported to be large. No quantitative data are available on garnet resources in the United States or other countries.

SOURCES OF STATISTICAL INFORMATION

The Bureau of Mines annually canvasses all known producers of garnet in the United States. The only source of information on foreign garnet production is its infrequent mention in Department of State dispatches, annual publications of the Colonial Geological Survey (United Kingdom), and the technical press. Exports are included with natural abrasives not elsewhere classified. Production of garnet paper and cloth is reported monthly by the Coated Abrasive Manufacturers' Institute.

PRODUCTION, CONSUMPTION, AND TRADE

Table 1 gives the tonnage and mine value of garnet mined in recent years in the United States. Output of finished product is virtually the same as sales.

TABLE 1.—*Abrasive garnet sold or used by producers in the United States*

Year	Short tons	Value (thousands)	Year	Short tons	Value (thousands)
1954–58 (average)	11,582	$1,037	1961	12,057	$1,036
1959	14,568	1,211	1962	14,166	1,172
1960	10,522	986	1963	14,626	1,412

In addition to New York and Idaho, domestic garnet production has been reported in the past from California, Connecticut, Florida, New Hampshire, North Carolina, and Pennsylvania. (*3*, *6*). It has been recovered from mill tailings near Bishop, Calif. Most of the world's garnet is produced in the United States. It is estimated that U.S.S.R. produces about 2,000 tons a year and that the combined production of Argentina, Australia, Malagasy Republic, Spain, Tanganyika, and Republic of South Africa does not exceed 1,000 tons annually.

Garnet is exported as graded material, but quantitative data are not available. No imports of industrial garnet were reported in 1963.

PRICES

The reported value of garnet ore ranges from $25 per ton for Idaho material to $140 for New York material. Finished New York abrasive garnet ranges from 12¾ cents per pound for powder in carload lots to 53 cents per pound for micron-size powder in retail lots. In many instances closely sized grain is more expensive than some powder. For example, a certain grade of powder, necessarily produced in milling, may sell for about 13 cents per pound and 240 to 280 mesh grain may be 22½ cents per pound.

TAXES

No special taxes are imposed on the garnet industry. Producers are granted a depletion allowance of 15 percent on domestic and foreign production.

RESEARCH

Research is conducted by Barton Mines Corp., especially in developing uses for finely ground garnet, which brings a premium price, and on better heat-treatment methods to improve the abrasive properties of garnet.

OUTLOOK

The currently producing garnet mines of the United States can fulfill foreseeable domestic market requirements and export demand at present market prices for this abrasive material. There is no prospect for the major domestic sources of supply to become exhausted. The good quality garnet in the extensive ore reserve at the Barton Mine in New York indicates an ample supply. The Idaho alluvial deposits contain a large tonnage of garnet which is available for sandblasting and similar uses in the Northwestern States. Byproduct garnet is accumulating from the milling of wollastonite, ilmenite, and other minerals at a rate faster than a market can be found for it, even at reduced prices.

New mining and milling methods may reduce the cost so that garnet can enter the field now held by lower-priced abrasives. Improved heat-treatment methods, combined with lower prices and more intensive sales effort, may offer garnet a chance to compete favorably with artificial abrasives and develop a wider market.

In the past 20 years the use of garnet increased about in equal proportion to the expansion of the entire abrasive industry. This trend seems likely to continue. The use of finely ground garnet and garnet powders in grinding and polishing compounds, nonskid paints and floor surfaces, spark-plug cleaning, and as a facing for building bricks has increased due to research and sales effort. While adding but little to the total tonnage of garnet sold, the higher prices that some special garnet products command increases materially its sales value.

Imported garnet does not compete with the domestic material, either in quality or price. Export of domestic garnet probably will continue, especially where a carefully processed material of good abrasive quality is needed.

A more intensive sales effort on the part of other abrasives may be the only action that would prevent the continued and possibly increased demand for garnet.

PROBLEMS

Garnet shares the overall problem of the abrasive industry in that it lacks a definitive and acceptable method of evaluating its abrasive qualities compared with other minerals and materials. Hardness, per se, does not assure that a material is a good abrasive. Other factors, including type of fracture, crystal form, friability, and ability to withstand heating also in part determine the abrasive value of a substance. Consequently, personal preferences and price often dictate the choice of abrasives.

The principal problems of the established garnet abrasive industry are maintenance of and means of increasing sales in the face of active competition from other abrasives. Numerous mineral operations are potential sources of byproduct garnet, but their development is usually limited as the market is adequately supplied with good-quality material from established sources. Local markets for abrasive used in nonskid pavements and paints might be developed near the sources of byproduct garnet.

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GEM STONES

By Benjamin Petkof [1]

GEM MATERIALS must have three principal qualities—beauty, durability, and rarity.

Gem stones are formed primarily by crystallization from aqueous solutions, crystallization from magmas, and metamorphism. Most economic deposits are in pegmatites, kimberlite pipes and dikes, and placers.

At least one variety of gem stone occurs in each State. More than 60 gem minerals, nearly all semiprecious, have been produced domestically, mostly from the Western States. In 1963 the U.S. gem stone production was valued at more than $1.4 million. Imports, mainly diamond, amounted to nearly $256 million. A prime feature of domestic production was the activity of amateur collectors, who collected, cut, and polished gems and manufactured jewelry as a hobby.

Virtually all gem stones are used for decorative purposes, mainly in jewelry but also for statuettes, vases, and other art objects, and for exhibit in private and public collections.

Materials used as substitutes for gem stones include plastics, glass, metals, and wood. Some synthetic gem stones compete with natural gems.

The price of a finished gem stone is determined primarily by its beauty, durability, rarity, freedom from defects, and perfection of cutting.

A chief problem of the domestic gem stone industry is lack of deposits of high-quality gem stones and low productivity in cutting and polishing compared with other countries.

BACKGROUND

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY (*8, 10, 28*)[2]

Only a few commercial mining firms are active in domestic gem stone production.

For the most part, production lies in the hands of numerous dedicated hobbyists and members of gem societies and clubs who spend their time and effort searching out interesting mineral deposits. Some collect only for the sake of mineral specimens; others cut and polish their finds into various crystal shapes and forms. Much of the trading consists of barter or exchange of specimens between collectors. Because of this situation, it is not possible to measure reliably the commercial magnitude of mining, processing, and trading of domestic gem stone.

More than 60 gem minerals, mostly semiprecious, have been produced commercially from domestic sources, and at least one variety of gem stone occurs in each State. About 87 percent of the total U.S. gem production, in order of decreasing value, comes from Oregon, California, Texas, Arizona, Nevada, Wyoming, Utah, Washington, Colorado, and Montana. The remaining production comes principally from other localities in the Rocky and Appalachian Mountains systems. Table 1 lists the principal gemstone localities in the United States.

World gem-diamond production comes mainly from Africa and South America. The principal producing countries are in Africa: Republic of South Africa, South-West Africa, Ghana, and Sierra Leone; in South America: Brazil, British Guiana, and Venezuela.

Foreign localities where major gem stone deposits, other than diamond, occur are: Australia (opal, beryl), Brazil (topaz, ruby, sapphire, beryl, agate), Burma (topaz, ruby, sapphire, beryl, jade), Ceylon (topaz, ruby, sapphire, beryl), Malagasy Republic (sapphire, tourmaline, rose quartz, beryl), and Mexico (topaz, opal, agate).

Such precious stones as diamond and emerald are imported in cut and uncut condition and

[1] Commodity specialist.
[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

distributed through jobbers and dealers. Cutting, polishing, and mounting is done by commercial lapidaries and jewelers in large industrial centers such as New York City. During 1963, imports of precious and semiprecious stones were valued at $256 million. About 2.8 million carats of cut and uncut diamonds were imported and represented about 88 percent of total imports by value.

Because of high labor costs, limited quantities of semiprecious stones are actually cut and polished in the United States. Most of this material is worked in nations where the cost of hand labor remains relatively low.

The Diamond Trading Co., Ltd., and the Industrial Distributors Ltd. market in excess of 90 percent of both gem and industrial diamond. These groups sell exclusively for the Diamond Corp. Ltd., which is under the control of DeBeers Consolidated Mines Ltd. and Consolidated Diamonds of South-West Africa. The Diamond Corp., through outright purchase or agreement, controls the sale and production of almost all large producers.

TABLE 1.—*Partial list of localities in the United States where gem materials have been reported found in 1953–63*

State and county	*Gem materials*
Alaska:[1]	
Cook Inlet-Susitna	Soapstone.
Northwestern Alaska	Jade.
Southeastern Alaska	Agate, garnet, jade.
Arizona:	
Apache	Agate, obsidian, peridot, petrified wood.
Cochise	Agate, amethyst, azurite, malachite, shattuckite.
Coconino	Agate, obsidian, petrified wood.
Gila	Agate, amethyst, azurite, bloodstone, carnelian, chalcedony, chrysocolla, epidote, garnet, hypersthene, obsidian, opal, peridot, pertified wood, serpentine, turquoise.
Graham	Agate, azurite, banded agate, chalcedony, malachite, obsidian, onyx, opal, pertified wood, turquoise.
Greenlee	Agate, amethyst, azurite, chalcedony, chrysocolla, garnet, jasper, malachite, obsidian, onyx, opal, petrified wood, rose quartz, shattuckite, turquoise, variscite.
Maricopa	Agate, amethyst, chalcedony, fire agate, jasper, marble, onyx, opal, petrified wood, plume agate.
Mohave	Agate, chalcedony, chalk turquoise, jasper, pertified wood.
Navajo	Garnet, petrified wood.
Pima	Azurite, chalcedony, malachite, obsidian, shattuckite.
Pinal	Chalcedony, chrysocolla, obsidian, peridot.
Yavapai	Agate, carnelian, chalcedony, chrysocolla, chrysoprase, jade, jasper, moonstone, obsidian, onyx, petrified wood, quartz crystal.
Yuma	Agate, chalcedony, garnet, jasper, obsidian, petrified wood, quartz crystal, rhyolite, turquoise.
Arkansas:	
Garland	Novaculite, quartz crystal.
Hot Spring	Quartz crystal, smoky quartz.
Montgomery	Quartz crystal.
Pike	Diamond.
California:	
Alameda	Agate.
Alpine	Do.
Amador	Rhodonite.
Calaveras	Agate, chalcedony, chrysoprase, petrified wood, quartz crystal.
Colusa	Travertine.
Contra Costa	Agate.
Del Norte	Agate, jasper, petrified wood.
El Dorado	Agate, garnet, idocrase, jasper, nephrite, petrified wood, vesuvianite.
Fresno	Chert, jasper, petrified wood, smoky quartz.
Humboldt	Agate, jade, jasper, petrified wood.
Imperial	Agate, andalusite, chalcedony, dumortierite, garnet, jasper, kyanite, opal, petrified palm root, petrified wood.
Inyo	Agate, amethyst, bloodstone, epidote, garnet, geode, jasper, obsidian, onyx, opal, quartz crystal, turquoise.
Kern	Actinolite, agate, colemanite crystal, jade, jasper, morrisonite, petrified wood, quartz crystal, rhodonite, rose quartz.
Lake	Jasper, onyx, quartz crystal.
Los Angeles	Agate, chalcedony, jasper, rhodonite.
Madera	Chiastolites.
Marin	Agate, jade, petrified whalebone.
Mariposa	Quartz crystal.
Mendocino	Agate, jade, jasper, opal, quartz.

[1] Alaska has no county designation.

TABLE 1.—*Partial list of localities in the United States where gem materials have been reported found in 1953–63*—Continued

State and county	Gem materials
California—Continued	
Modoc	Agate, jasper, obsidian.
Mono	Geode, obsidian.
Monterey	Agate, jadeite, jasper, nephrite, rhodonite, serpentine.
Napa	Cinnabar, jasper, onyx, quartz crystal.
Nevada	Opal, petrified wood.
Placer	Jade.
Riverside	Actinolite, agate, amazonite, aquamarine, beryl, calcite, chalcedony, corundum, diopside, epiodote, fire agate, garnet, geode, idocrase, jasper, petrified wood, quartz crystal, rhodonite, rose quartz, rubellite, spinel, topaz, tourmaline.
Sacramento	Agate, jade, opal.
San Benito	Benitoite, diopside, garnet, jade, jadeite, natrolite, serpentine.
San Bernardino	Actinolite, agate, amethyst, aragonite, bloodstone, chalcedony, crawfordite, epidote, geode, jasper, moss agate, onyx, opalite, petrified wood, rhodonite, travertine, verde antique.
San Diego	Beryl, garnet, kunzite, quartz crystal, rhodonite, topaz, tourmaline.
San Francisco	Jasper, nephrite.
San Luis Obispo	Agate, jade, jasper, marcasite, onyx, quartz, sagenite.
San Mateo	Petrified whalebone.
Santa Barbara	Agate.
Santa Clara	Agate, jasper.
Santa Cruz	Agate, petrified whalebone.
Siskiyou	Agate, californite, idocrase, jade, quartz crystal, rhodonite.
Solano	Onyx, travertine.
Sonoma	Actinolite, jasper.
Trinity	Agate, jade, jasper, rhodonite.
Tulare	Agate, chrysoprase, jade, quartz crystal, smoky quartz, thulite, topaz.
Tuolumne	Agate, gold quartz, jasper, marble, petrified wood, pyrite.
Ventura	Agate.
Colorado:	
Chaffee	Agate, aquamarine, beryl, jasper, onyx, petrified wood, phenacite.
Clear Creek	Amazonite, garnet.
Custer	Petrified wood.
Delta	Jasper.
Douglas	Amazonite, smoky quartz, topaz, petrified wood.
Elbert	Petrified wood.
El Paso	Agate, amazonite, garnet, phenacite, topaz, tourmaline, zircon.
Fremont	Agate, coprolite, onyx, petrified wood, rose quartz, satin spar.
Garfield	Oil shale, petrified wood.
Jefferson	Amazonite, barite crystal, beryl, topaz, tourmaline.
Kiowa	Agate.
Las Animas	Rose agate.
Mesa	Agate, amethyst, flint, petrified wood.
Mineral	Agate, amethyst, jasper, petrified wood.
Moffat	Agate.
Montrose	Amazonite, coprolite, covellite, jasper, phenacite, smoky quartz, topaz.
Ouray	Quartz crystal, rhodonite.
Park	Agate, beryl, fluorite, jade, moss opal, petrified wood, topaz.
Rio Grande	Agate, petrified wood.
Saguache	Agate, amethyst, jade, turquoise.
San Juan	Feldspar, mica, quartz crystal, rhodonite.
San Miguel	Jasper, petrified bone.
Sedgwick	Agate, petrified wood.
Teller	Agate, amazonite, amethyst, jade, petrified wood, phenacite, quartz crystal siderite, smoky quartz, topaz, zircon.
Weld	Agate, barite, petrified wood.
Connecticut:	
Fairfield	Albite, beryl, epidote, fluorite, mica, quartz crystal, scheelite, siderite, spodumene, topaz, tremolite, wolframite.
Hartford	Amethyst, azurite, datolite, malachite, phrenite, quartz, smoky quartz.
Litchfield	Calcite, fluorite, galena, garnet, graphite, kyanite, magnetite, opal, prehnite, pyrite, quartz, siderite, sphalerite, stilbite, tourmaline, tremolite.
Middlesex	Actinolite, amblygonite, apatite, austinite, bertrandite, beryl, columbite, chrysoberyl, feldspar, fluorite, garnet, hiddenite, kunzite, lepidolite, mica, pollucite, rose quartz, spodumene, topaz, tourmaline.
New Haven	Amethyst, barite, beryl, columbite, datolite, feldspar, garnet, phrenite, rose quartz, smoky quartz.
New London	Garnet, kyanite, pyrite, quartz crystal, rose quartz.
Florida:	
Hillsborough	Agatized coral.
Pinellas	Agatized shark bone.

TABLE 1.—*Partial list of localities in the United States where gem materials have been reported found in 1953–63*—Continued

State and county	*Gem materials*
Georgia:	
Brooks	Agate.
Cobb	Topaz.
Elbert	Smoky quartz.
Forsyth	Moonstone.
Habersham	Kyanite.
Jones	Agate.
Lincoln	Lazulite, rutile.
Lumpkin	Garnet.
Morgan	Amethyst.
Paulding	Garnet.
Rabun	Amethyst, garnet, quartz, rose quartz, ruby.
Towns	Ruby, sapphire.
Troup	Amethyst, aquamarine, rose quartz.
Washington	Opal.
Wilkes	Kyanite, lazulite, rutile.
Idaho:	
Benewah	Garnet.
Blaine	Agate, petrified wood.
Butte	Do.
Canyon	Agate, petrified wood, white plume agate.
Lemhi	Petrified wood.
Nez Perce	Agate, garnet, jasper, opal, petrified wood, sapphire.
Owyhee	Agate, jasper, petrified wood.
Illinois: Hancock	Geode.
Iowa:	
Des Moines	Do.
Henry	Agate, jasper, petrified wood.
Lee	Geode, jasper.
Muscatine	Agate.
Page	Do.
Kansas:	
Cherokee	Marcasite, sphalerite.
Franklin	Petrified wood.
Wallace	Opal.
Wyandotte	Agate.
Louisiana:	
Ouachita	Agate, jasper, petrified wood.
Vernon	Petrified wood.
Maine:	
Androscoggin	Amblygonite, apatite, beryl, garnet, lepidolite, spodumene, pollucite, tourmaline.
Cumberland	Actinolite, beryl, columbite, garnet.
Franklin	Columbite, spondumene.
Hancock	Beryl.
Kennebec	Cancrinite, nephelite, sodalite, zircon.
Knox	Spodumene.
Oxford	Agate, amblygonite, amethyst, apatite, aquamarine, beryl, chrysoberyl, eosphorite, herderite, lepidolite, pollucite, quartz crystal, rose quartz, smoky quartz, spodumene, tourmaline.
Sagadahoc	Beryl, lepidolite, tourmaline.
Washington	Agate, jasper.
Maryland:	
Allegany	Barite crystal, quartz crystal, siderite.
Baltimore	Antigorite, calcite crystal, garnet, jasper, quartz, serpentine, smoky quartz, tourmaline.
Calvert	Jasper.
Carroll	Azurite, malachite.
Cecil	Onyx, serpentine, williamsite.
Frederick	Onyx, malachite.
Garrett	Picrolite, serpentine, williamsite.
Hartford	Serpentine.
Washington	Cuprite.
Massachusetts:	
Hampden	Amethyst, beryl, datolite, marcasite, phrenite.
Hampshire	Amethyst, beryl, datolite, galena, phrenite, pollucite, spodumene.
Middlesex	Scheelite.
Worcester	Beryl, chiastolite, spodumene.
Michigan:	
Dickinson	Actinolite.
Emmet	Agate, fossils, petoskey stone.
Houghton	Agate, garnet.

TABLE 1.—*Partial list of localities in the United States where gem materials have been reported found in 1953–63*—Continued

State and county	*Gem materials*
Michigan—Continued	
Keweenaw	Agate, chlorastrolite, domeykite, thomsonite.
Marquette	Jasper, jaspillite.
Ontonagon	Agate, datolite, malachite, tenorite.
Minnesota:	
Carlton	Agate, jasper.
Cook	Agate, heulandite.
Lake	Agate, thomsonite.
Morrison	Garnet, staurolite.
Pipestone	Catlinite.
St. Louis	Agate.
Winona	Do.
Mississippi:	
Harrison	Jasper.
Wayne	Petrified wood.
Missouri:	
Bollinger	Agate, jasper.
Cape Girardeau	Do.
Clark	Geode.
Crawford	Amethyst.
Franklin	Do.
Jackson	Do.
Lewis	Agate.
Madison	Agate, jasper.
St. Louis	Agate, barite, galena, geode.
Wayne	Agate, jasper.
Montana:	
Beaverhead	Corundum, quartz.
Custer	Agate, sapphire.
Dawson	Agate.
Deer Lodge	Sapphire.
Fergus	Do.
Gallatin	Agate, corundum, petrified wood, rose quartz.
Granite	Sapphire.
Jefferson	Amethyst, barite, tourmaline.
Judith Basin	Sapphire.
Lewis and Clark	Garnet, ruby, sapphire, spinel.
Madison	Garnet, jasper, onyx, orthoclase, quartz crystal, serpentine, tourmaline.
Meagher	Agate.
Missoula	Quartz.
Park	Amethyst, arsenopyrite, garnet, iceland spar, petrified wood, travertine.
Powell	Agate, amazonite, sapphire.
Prairie	Agate, petrified wood.
Ravalli	Fluorite.
Rosebud	Agate.
Silver Bow	Amethyst, epidote, fluorite, garnet, sapphire.
Yellowstone	Agate, jasper.
Nebraska:	
Cass	Horn coral, petrified wood.
Dawes	Chalcedony.
Gage	Geode.
Jefferson	Agate, jasper, petrified wood.
Lincoln	Agate, jasper.
Nance	Agate, jasper, petrified wood.
Saunders	Agate, petrified wood.
Sioux	Agate, chalcedony, petrified wood.
Nevada:	
Clark	Amethyst.
Douglas	Topaz.
Elko	Agate, azurite, chalcedony, petrified wood.
Esmeralda	Agate, chalcedony, petrified wood, turquoise.
Eureka	Sulfur crystal.
Humboldt	Agate, fire opal, jasper, petrified wood, rhodonite.
Lander	Chert, turquoise.
Lincoln	Agate, chalcedony, chrysocolla, jasper, malachite, petrified wood, quartz.
Lyon	Agate, jasper, opal.
Mineral	Obsidian, petrified wood, turquoise.
Nye	Onyx, petrified wood.
Pershing	Opal, petrified wood.
Washoe	Agate, garnet, idocrase, jasper, obsidian, petrified wood, piedmontite.
White Pine	Garnet.

TABLE 1.—*Partial list of localities in the United States where gem materials have been reported found in 1953–63*—Continued

State and county	*Gem materials*
New Hampshire:	
Carroll	Amethyst, danalite, phenacite, helvite, quartz crystal, smoky quartz, topaz.
Cheshire	Amethyst, apatite, aquamarine, beryl, fluorite, garnet, quartz crystal, rose quartz, tourmaline, spodumene.
Coos	Amethyst, quartz crystal, topaz.
Grafton	Apatite, beryl, columbite.
Merrimack	Beryl, garnet.
Rockingham	Spodumene.
Sullivan	Aquamarine, rose quartz.
New Jersey:	
Bergen	Natrolite.
Cape May	Jasper, quartz crystal.
Mercer	Albite, calcite, chabazite, datolite, natrolite, stilbite.
Middlesex	Marcasite, petrified wood, pyrite.
Morris	Carnelian, serpentine.
Passaic	Agate, amethyst, carnelian, chabazite, datolite, heulandite, pectolite, prehnite.
Sussex	Aragonite, corundum, garnet, pyrrhotite, rhodonite, spinel, tourmaline, willemite.
Union	Calcite, chalcedony, prehnite, sphalerite, stilbite.
Warren	Molybdenite
New Mexico:	
Bernalillo	Agate.
Catron	Do.
Chaves	Do.
Eddy	Agate, quartz crystal.
Grant	Agate.
Hidalgo	Agate, chalcedony, serpentine.
Luna	Agate, carnelian, onyx, travertine.
Otero	Turquoise.
Rio Arriba	Agate beryl, dumortierite, feldspar, petrified wood.
San Juan	Agate, ricolite, petrified wood.
Santa Fe	Beryl.
Sierra	Agate, carnelian, fluorite, petrified wood.
Socorro	Agate, chalcedony.
Valencia	Agate, jasper, obsidian, petrified wood.
New York:	
Dutchess	Quartz crystal.
Erie	Satin spar.
Essex	Garnet, rose quartz, wollastonite.
Herkimer	Quartz crystal.
Jefferson	Hematite.
Madison	Celestite.
Niagara	Calcite.
Orange	Quartz crystal, sunstone, tourmaline.
Putnam	Magnetite, opal, serpentine.
Rockland	Pink garnet, sphene.
St. Lawrence	Calcite, hexagonite, pyrite, serpentine, sphalerite, talc, tremolite.
Saratoga	Beryl.
Ulster	Quartz crystal.
Warren	Garnet.
Westchester	Beryl, garnet, quartz, rose quartz.
North Carolina:	
Alexander	Hiddenite, quartz, rutile, sapphire.
Ashe	Beryl, garnet, moonstone, rutile.
Avery	Epidote, unakite.
Buncombe	Kyanite, moonstone.
Burke	Amethyst.
Clay	Ruby, sapphire.
Granville	Jasper.
Haywood	Emerald, sapphire.
Iredell	Actinolite, rose quartz, sapphire.
Macon	Garnet, rhodonite, ruby, sapphire.
Mitchell	Actinolite, beryl, biotite, emerald, epidote, feldspar gems, garnet, rhodonite, unakite.
Orange	Agate.
Rutherford	Emerald.
Warren	Amethyst.
Wilkes	Agate.
Yancey	Emerald, feldspar gems.

TABLE 1.—*Partial list of localities in the United States where gem materials have been reported found in 1953–63*—Continued

State and county	*Gem materials*
North Dakota:	
Adams	Petrified wood.
Billings	Do.
McLean	Do.
Morton	Do.
Stark	Chalcedony, jasper, quartz crystal.
Ohio:	
Coshocton	Flint, selenite crystal.
Franklin	Petrified wood.
Gallia	Do.
Licking	Flint, jasper.
Lucas	Fossils.
Montgomery	Agate, gem granite.
Muskingum	Jasper.
Ottawa	Celestite, fluorite.
Wood	Barite, calcite.
Oklahoma:	
Canadian	Agate, jasper, petrified wood.
Comanche	Zircon.
Dewey	Agate, chalcedony, jadite, jasper, petrified wood.
Greer	Alabaster.
Jackson	Quartz.
Major	Agate, jasper, petrified wood.
Ottawa	Sphalerite.
Pushmataha	Green quartz.
Oregon:	
Baker	Agate, jasper, petrified wood.
Benton	Agate.
Coos	Fossil wood.
Crook	Agate, carnelian, geode, moss agate.
Curry	Jade.
Deschutes	Agate, carnelian, geode, jasper, moss agate.
Douglas	Agate.
Grant	Agate, petrified wood.
Harney	Agate, obsidian.
Jackson	Agate, bloodstone, jasper, petrified wood, rhodonite.
Jefferson	Agate, amethyst, geode, opal.
Lake	Geode, obsidian.
Lane	Agate, petrified wood.
Lincoln	Agate, agatized coral, bloodstone, jasper, petrified wood, sagenite, sardonyx.
Linn	Agate.
Malheur	Agate, geode, jasper, petrified wood.
Morrow	Agate, geode.
Polk	Agate, jasper, petrified wood.
Union	Agate.
Wallowa	Do.
Wasco	Agate, amethyst, bloodstone, chalcedony, geode, jade, jasper, opal, quartz, sagenite.
Wheeler	Agate.
Pennsylvania:	
Adams	Cuprite.
Bedford	Calcite, quartz, spar.
Berks	Calcite, epidote, feldspar, garnet, hematite, kyanite, magnetite, quartz crystal, unakite, zeolite.
Bucks	Galena, sphalerite.
Carbon	Autunite, carnotite.
Chester	Anglesite, azurite, feldspar, garnet, goethite, hornblend, kyanite, magnetite, malachite, martite, phlogopite, pyromorphite, pyrite, pyrrhotite, quartz, quartz crystal, sphalerite, sulfur, stibnite, wulfenite.
Cumberland	Phosphorite.
Delaware	Actinolite, apatite crystal, deweylite, feldspar, garnet.
Lancaster	Actinolite, aragonite, calcite, chalcedony, chromite, dolomite, hematite, malachite, marcasite, quartz crystal, pyrite, serpentine.
Lebanon	Anthophyllite, apophylite, biotite, garnet, hematite, magnetite, serpentine.
Lehigh	Calamine, corundum, goethite, greenockite, jasper, quartz crystal, sphalerite.
Monroe	Quartz crystal.
Montgomery	Calcite, galena, lead and copper minerals, natrolite, quartz crystal, sphalerite, stibnite, zeolite.
Northampton	Calcite, graphite, gummite, limonite, serpentine, talc, uraninite.
Perry	Travertine.

TABLE 1.—*Partial list of localities in the United States where gem materials have been reported found in 1953–63*—Continued

State and county	*Gem materials*
Pennsylvania—Continued	
Schuylkill	Chlorite, galena, pyrite, quartz crystal, siderite, sphalerite.
Somerset	Quartz.
Westmoreland	Petrified wood, quartz.
York	Limonite, pyrite.
Rhode Island: Providence	Amethyst, beryl, fluorite, quartz crystal.
South Carolina:	
Anderson	Tourmaline.
Chesterfield	Topaz.
Florence	Petrified wood.
South Dakota:	
Custer	Agate, amblygonite, beryl, chalcedony, feldspar, garnet, jade, jasper, lepidolite, mica, petrified wood, quartz crystal, rose quartz, sillimanite, tourmaline.
Fall River	Agate, chalcedony, jasper, petrified wood, vanadanite.
Harding	Agate, petrified wood.
Lawrence	Garnet, rose quartz.
Meade	Gastroliths, geode, petrified wood, selenite.
Pennington	Agate, apatite, beryl, chalcedony, feldspar, galena, garnet, jasper, lepidolite, petrified wood, rose quartz, staurolite, tourmaline.
Shannon	Agate, jasper, petrified wood.
Tennessee:	
Bedford	Agate.
Carter	Unakite.
Coffee	Agate.
Texas:	
Brewster	Agate, amethyst, carnelian, chalcedony, citrine, fire opal, jasper, labradorite, moonstone, novaculite, petrified wood, quartz.
Burnet	Garnet, topaz.
Culberson	Agate.
De Witt	Agate, jasper, petrified wood.
Duval	Do.
El Paso	Agate.
Fayette	Petrified wood.
Gillespie	Amythest, garnet, petrified wood, topaz.
Gonzales	Petrified wood.
Hidalgo	Agate.
Hudspeth	Do.
Jeff Davis	Adularia, agate, amethyst, carnelian, chalcedony, citrine, jasper, moonstone, opal, petrified wood, quartz crystal.
Lee	Petrified wood.
Live Oak	Agate, petrified wood.
Llano	Amethyst, garnet, quartz crystal, topaz, tourmaline.
McMullen	Petrified wood.
Mason	Amazonite, cassiterite, fluorite, quartz, topaz.
Pecos	Agate.
Potter	Petrified wood.
Presidio	Agate, amethyst, carnelian, chalcedony, citrine, jasper, moonstone, opal, petrified wood, quartz crystal.
Reeves	Do.
Taylor	Smoky quartz, topaz.
Terrell	Agate.
Travis	Topaz.
Trinity	Petrified wood.
Walker	Do.
Webb	Agate, jasper.
Zapata	Do.
Utah:	
Beaver	Agate, obsidian, quartz crystal.
Box Elder	Variscite.
Carbon	Agate.
Emery	Agate, chalcedony, obsidian, petrified wood.
Garfield	Agate, barite, dinosaur bone, onyx, petrified wood, jasper.
Grand	Agate, dinosaur bone, petrified wood, jasper.
Iron	Agate, geode.
Juab	Agate, geode, jasper, topaz.
Kane	Agate, petrified wood.
Millard	Fossils, jasper, obsidian.
Salt Lake	Agate, onyx.
Sevier	Agate.
Tooele	Agate, geode, obsidian.
Utah	Onyx, variscite.
Washington	Agate, alabaster, azurite, jasper.
Wayne	Agate, barite, dinosaur bone, jasper, petrified wood.

TABLE 1.—*Partial list of localities in the United States where gem materials have been reported found in 1953–63*—Continued

State and county	*Gem materials*
Vermont: Windsor	Actinolite, magnetite, pyrite, talc.
Virginia:	
Amelia	Albite, amazonite, cleavelandite, garnet.
Madison	Blue quartz, epidote, unakite.
Page	Epidote, jasper, onyx.
Prince Edward	Amazonite, amethyst, kyanite.
Rockbridge	Unakite.
York	Shark teeth, whalebone.
Washington:	
Benton	Petrified wood.
Chelan	Thulite.
Cowlitz	Carnelian, sardonyx.
Douglas	Jadeite, thulite.
Kittitas	Agate, chalcedony, jasper, petrified wood.
Klickitat	Agate, jasper, petrified wood.
Lewis	Carnelian, sardonyx.
Snohomish	Petrified wood.
Yakima	Carnelian, sardonyx.
West Virginia:	
Hardy	Aragonite, stilbite.
Mineral	Fossils.
Wisconsin:	
Ashland	Agate, jasper.
Bayfield	Agate.
Clark	Agate, jasper.
Douglas	Agate.
Iron	Do.
Wyoming:	
Albany	Agate, petrified wood.
Big Horn	Agate.
Carbon	Agate, jade, jasper, petrified wood.
Fremont	Actinolite, agate, aventurine, garnet, jade, jasper, petrified wood, rhodonite, sapphire, serpentine.
Goshen	Jasper.
Johnson	Petrified wood.
Lincoln	Agate, petrified wood.
Natrona	Agate, amazonite, jade, petrified wood.
Platte	Agate.
Sweetwater	Agate, chalcedony, corundum, eden wood, jade, jasper, moss agate, petrified wood.
Uinta	Petrified wood.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Rocks, mineral specimens, and certain organic materials, such as pearl, amber, jet, and coral, are included in gem stone statistics but are not covered in this chapter.

There is no sharp distinction between precious and semiprecious gems. In this chapter diamond, ruby, sapphire, and emerald are considered precious stones and all other gems semiprecious.

Gem stones must have qualities of splendor or beauty, durability, and rarity. Splendor in a gem depends upon transparency, brilliance, luster, and color. Luster is a function of the transparency, refractivity, and crystal structure of a mineral; durability is determined by hardness and toughness; and rarity is a major factor in determining the value of a gem.

Of the 1,500 mineral species, only about 100 have all of the attributes required in gems (*16*). Of these, the silicates furnish the greatest number, including beryl (emerald and aquamarine), tourmaline, topaz, and quartz (agate, chalcedony, and opal). Oxides, such as corundum (ruby and sapphire), comprise the second largest group. Sulfides, carbonates, phosphates, and sulfates are of little importance. The most important commercial gem stone, diamond, is an element (carbon). Other elements used as gem materials include native gold, copper, and silver.

Gem materials are classified into group, species, and variety (*4*). Group refers to two or more gem minerals that are similar in crystal structure and physical properties but have different chemical properties. The individual members of the group are the species. Varieties of a species have similar crystal structure and chemical characteristics but differ in color.

TECHNOLOGY

Geology

The large number of gem minerals implies a variety of occurrences and origins (*24, 30*).

Gem minerals are formed principally by precipitation from aqueous solutions, crystallization from magmas, and metamorphic processes.

Many gem stones, including beryl, tourmaline, topaz, spodumene, and quartz, are formed in igneous rocks, principally pegmatites. Kimberlite pipes and dikes are the major sources of diamond. Emerald and garnet occur in metamorphic rocks.

Most gems are dense, resistant to abrasion, and chemically inert. Ruby, sapphire, tourmaline, agate, jade, zircon, diamond, garnet, and quartz are obtained commercially from alluvial deposits.

Mining

Gem stone mining in the United States consists essentially of the activities of thousands of amateur "rockhounds." Most gems are mined with hand picks and shovels and are hand sorted.

Some owners of gem stone claims use power-operated dirt-moving equipment to uncover the gem material and open their land to collectors for fees. In some localities the uncovered material is screened and washed by panning; in other areas the gem-bearing material is sorted directly by hand.

Gem stone placer-mining methods are similar to those used in gold placer mining. In the better equipped mines the topsoil is stripped with bulldozers and wheel scrapers, and the gem-bearing gravel is treated in washing plants. The final separation is made with grease tables, electrostatic separators, and hand picking (*21*, *29*).

Underground mining methods are used in the diamond "pipe" mines of South Africa. The ore is crushed and concentrated by heavy-medium separation, concentrating pans, and jigs. The final separation is done on grease tables (*15*).

Diamond-bearing gravel deposits in shallow coastal waters off the South-West African coast are mined by suction dredge and the gravel pumped to a shipboard plant where it is beneficiated and the diamond recovered (*6*, *17*).

Cutting and Polishing

Usually amorphous and cryptocrystalline gem materials are cut or carved and polished as shown in figure 1.

Cutting of cabochons comprises four main operations, sawing, grinding, sanding, and polishing (*1*). Sawing is done when cutting large, rough masses or preliminary to polishing large, flat surfaces. Two general methods are "mud" sawing with a creamy mixture of silicon carbide powder, water, and glycerin and "diamond charged" sawing with a mixture of diamond dust and oil. Grinding is accomplished by using different grades of grinding wheels, depending upon the hardness of the gem material. Sanding removes the large scratches made in grinding. Disk, belt, or drum sanders, made of felt cloth or canvas coated with an abrasive grit such as silicon carbide and aluminum oxide, are used. Polishing is usually done on a revolving hard-felt lap or muslin or leather buff, in either horizontal or vertical position. Polishing agents include tin oxide, tripoli, cerium oxide, alumina, and rouge.

Tumbling, an inexpensive method of polishing gems of irregular shape, is done in lined and unlined containers, using a polishing medium with or without water (*30*). The irregular shapes produced are called baroque gems.

Some precious gems are beautiful in their natural form, but usually their appearance is improved by cutting and polishing in one or more of the cuts shown in figure 2.

Facet cutting is confined mainly to transparent gems having a hardness of 7 or more. The "brilliant" cut, most commonly used in faceting, has 58 facets, 33 above the circle "girdle" and 25 below it, arranged in eightfold symmetry. (See fig. 1.)

Manufacture of Synthetic Gems

The flame-fusion process, developed by Verneuil in 1902, made possible the synthesis of ruby and later of sapphire, spinel, rutile, and beryl. This process consists of growing a single crystal in a simple, inverted, oxyhydrogen blowpipe. In manufacturing synthetic gems, pure oxides of aluminum and titanium and, sometimes, coloring oxides are charged at the top of a small furnace and melted as they pass through an oxygen-hydrogen flame. The molten alumina is solidified on a fire-clay peg as a carrot-shaped crystal known as a boule, usually ½ to 1 inch in diameter, 2 to 4 inches long, and weighing 75 to 250 carats. The boule is then heat-treated or split to relieve the inherent strain, cut, and polished into gems.

Other processes used to synthesize gem materials include—

1. Crystal growth from solution (quartz, beryl, sapphire, garnet).
2. Solid-state reaction and phase transformation (lapis lazuli).
3. Vapor-phase reaction (greenockite, marcasite).
4. High temperature and pressure (ruby, sapphire, diamond).

A guide to the various stones used in jewelry is given in table 2.

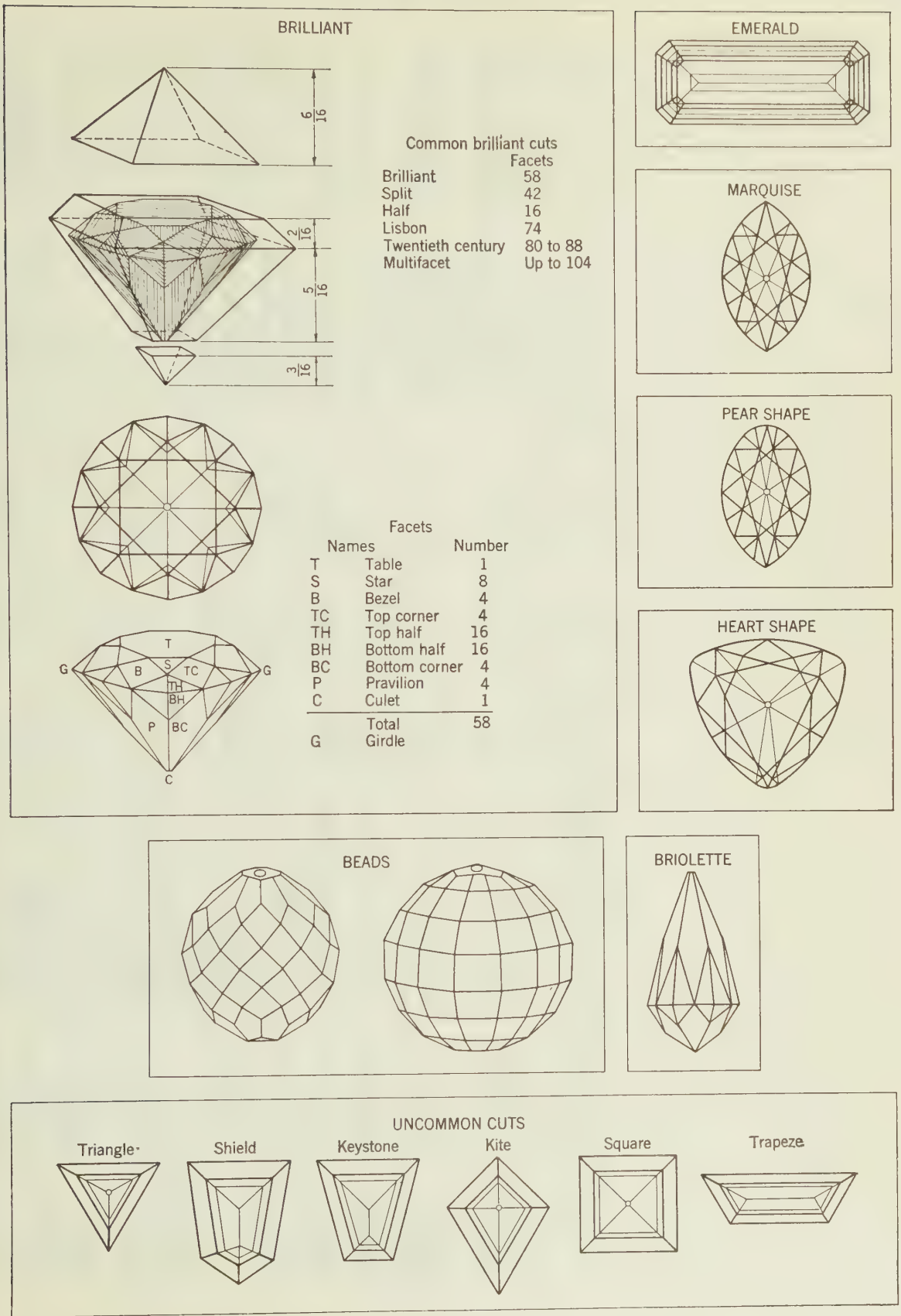

FIGURE 1.—Principal Forms of Crystalline Gem-Stone Cuts.

TABLE 2.—*Reference guide to the various stones used in jewelry*

Name	Composition	Color	Resistance to wear	Practical size [1]	Cost [2]	Refraction	Refractive index	May be confused with—	Recognition characters
Beryl:									
Aquamarine	Beryllium aluminum silicate.	Blue-green to light blue.	Good	Any	Medium	Double	1.58	Synthetic spinel, blue topaz.	Double refraction, refractive index.
Emerald	do	Green	Poor	Medium	Very high	do	1.58	Soldered emerald, glass, tourmaline, peridot, green garnet.	Emerald filter dichroism, refractive index.
Emerald (synthetic).	do	do	do	Very small	High	do	1.58	Genuine emerald	Flaws, brilliant fluorescence in ultraviolet light.
Golden	do	Yellow to golden	Good	Any	Medium	do	1.58	Quartz topaz, precious topaz, glass, doublets.	Refractive index, double refraction.
Morganite	do	Pink to rose	do	do	Low to medium.	do	1.58	Kunzite, tourmaline, pink sapphire.	Refractive index.
Chrysoberyl:									
Alexandrite	Beryllium silicate	Green by day, red by artificial light.	do	Russian (small); Ceylon (medium).	High	do	1.75	Synthetic	Dichroism, inclusions in synthetic sapphire.
Catseye	do	Greenish to brownish	Excellent	Small to large	do	do	1.75	Quartz	Gravity and translucence.
Chrysolite	do	Yellow, green, brown.	Good	Medium	Medium	do	1.75	Tourmaline, peridot	Refractive index, silky.
Corundum:									
Ruby	Aluminum oxide	Rose to deep purplish red.	do	Small	Very high	do	1.78	Synthetic	Inclusions and shape of flaws.
Sapphire	do	Blue	do	Medium	High	do	1.78	Synthetics including spinel.	Inclusions, double refraction, dichroism.
Sapphire (fancy)	do	Yellow, pink, white, orange, green, violet.	do	Medium to large.	Medium	do	1.78	Synthetics, glass and doublets.	Inclusions, double refraction, refractive index.
Sapphire and ruby stars.	do	Red, pink, violet, blue, gray.	do	do	High to low	do		Star quartz, synthetic stars.	Shows asterism, color on side view.
Sapphire or ruby (synthetic).	do	Yellow, pink, blue, red, white, green, violet.	do	Up to 20 carats	Low	do	1.78	Synthetic spinel, glass	Double refraction, refractive index.
Diamond	Carbon	White, blue-white, yellow, brown, green, red, blue, pale.	Excellent	Any	High	Single	2.42	Zircon, titania	High index, dispersion, single refraction, hardness, cut, luster.
Feldspar:									
Amazonstone	Alkali aluminum silicate.	Green	Fair	Large	Very low			Jade	Cleavage sheen, vitreous to pearly, opaque.
Labradorite	do	Gray with blue sheen	do	do	do			Brazilian butterfly	Do.
Moonstone	do	White	do	do	do		1.52	Glass or white onyx	Blue sheen, opalescent.
Garnet	Variable silicate	Brown, black, yellow, green, ruby red.	Good to fair	Small to medium.	Low to medium.	Double (strong).	1.79–1.98	Synthetics, spinel, glass.	Double refraction, wear on facet edges, light-colored varieties are transparent.
Jade	Complex silicate	Green, red, black, white, mauve.	Good	Large	Low to very high.		1.65–1.68	Onyx or glass	Luster of polished surface, translucent to opaque.

Olivine: Peridot	Iron magnesium silicate.	Yellow, green	Fair	Any	Medium	Double (strong).	1.68	Tourmaline, chrysoberyl.	Strong double refraction, low dichroism.
Opal	Hydrous silica	Colors flash in white, gray, black, red, yellow.	Poor	Large	Low to high	Single	1.45	Glass	Color changes.
Quartz:									
Agate	Silica	Any colors	Good	do	Low			do	Crystalline, irregularly banded.
Amethyst	do	Purple	do	do	Medium	Double	1.55	do	Refractive index and double refraction, transparent.
Cairngorm	do	Smoky	do	do	Low	do	1.55	do	Do.
Citrine	do	Yellow	do	do	do	do		do	Do.
Crystal (rock)	do	Colorless	do	do	do	do	1.55	do	Do.
Jasper	do	Uniform or spotted, red, yellow, brown, green, blue.	do	do	do			do	Opaque, vitreous.
Onyx	do	Many colors	do	do	do			do	Uniformly banded.
Rose	do	Pink, rose red	do	do	do	do	1.55	do	Refractive index and double refraction, transparent.
Spinel	Magnesium aluminum oxide.	Red, blue, lilac, orange, yellow, purple, green.	Medium	Medium	Low to medium.	Single	1.72	Synthetic sapphire, garnet.	Refractive index, single refraction, inclusions.
Spinel (synthetic)	do	Blue, white, light blue, yellow, gray, green, alexandrite colors.	Good	Up to 40 carats	Low	Double	1.73	Spinel, sapphire, aquamarine, topaz, alexandrite.	Weak double refraction, lack of dichroism, refractive index.
Spodumene:									
Kunzite	Lithium aluminum silicate.	Pink to lilac	Poor	Any	Medium	Double	1.66	Pale amethyst, morganite.	Refractive index, transparent.
Hiddenite	do	Yellow to green	do	do	do	do	1.66	Synthetic spinel	Do.
Topaz (precious)	Complex silicate	White, blue, yellow, pink, red, green.	Fair	White and blue any size. Yellow and pink to medium.	Low to medium.	do	1.62	Beryl, aquamarine, quartz, topaz.	Refractive index.
Tourmaline	do	Red, pink, green, blue, wine, brown, yellow.	do	Green and red to 50 carats. Others medium.	do	do	1.63	Peridot, beryl, corundum, glass.	Double refraction, refractive index.
Turquoise	Copper aluminum phosphate.	Blue to green	do	Large	Low	do	1.63	Glass or composition	Difficult if matrix not present, matrix usually limonitic.
Zircon	Zirconium silicate	White, blue, brown, yellow, green.	Poor	Small to medium.	Low to medium.	Double (strong).	1.79–1.98	Diamond, synthetics	Double refraction, wear on facet edges.

[1] Small—up to 5 carats; medium—up to 50 carats; large—over 50 carats.
[2] Low—up to $5 per carat; medium—up to $100 per carat; high—over $100 per carat.

Source: Modified from Jewelers' Circular-Keystone, v., 123, No. 6, March 1953, p. 101.

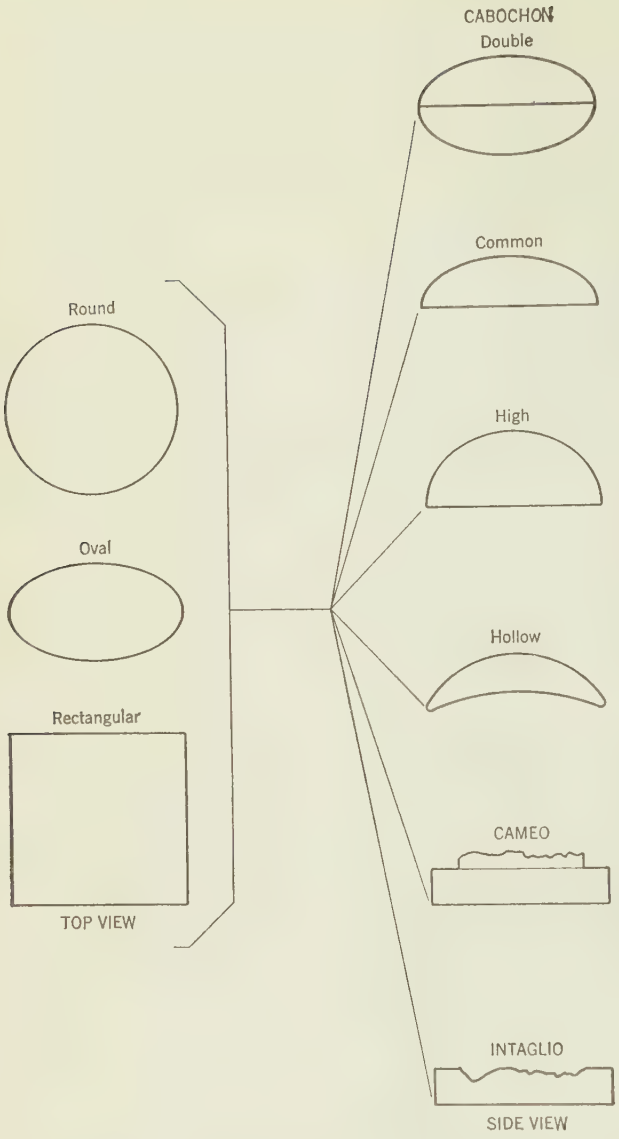

FIGURE 2.—Cryptocrystalline Gem-Stone Cuts.

The color of many natural stones may be changed by heating, dyeing, or exposure to X-rays, cyclotron bombardment, deuteron bombardment in nuclear reactors, or cathode rays (*7*, *25*).

USES

Virtually all gem stones are used for decorative purposes in jewelry, for statuettes, vases, and other art objects, and for exhibit in collections.

Some low-quality gem diamond is used as industrial diamond when the value is about the same. Tourmaline is used as a simple laboratory polariscope, as a piezoelectric material, and in gages for measuring extremely high pressures. Agate is made into mortar and pestle sets, knife edges for balances, textile rollers, and spatulas. Originally, ultramarine blue pigment was made from lapis lazuli. Other gem materials are or have been used by industry for minor applications.

Many people purchase precious stones because they represent concentrated wealth that can easily be transported, hidden, and sold or traded.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Beryl, tourmaline, spodumene, and gem quartz occasionally are coproducts of mica, feldspar, quartz, and other pegmatite minerals. Gem-quality diamond is a coproduct of industrial diamond at most mines. Frequently, gem stones are byproducts of other commodities. For example, diamond has been recovered from gold dredges, turquoise from copper mines, agate and petrified wood from gravel pits, and gem garnet from abrasive garnet operations.

ALTERNATE MATERIALS

Plastics, glass, metals, wood, paper, and other materials are substituted for gem stones in costume jewelry. Natural gems having little color are made to appear darker by cementing colored glass on a natural stone.

Many synthetic gem stones compete with natural gems. They include ruby, sapphire, spinel, rutile, and emerald. Industrial diamond also is manufactured, but crystals large enough for gems have yet to be produced.

SECONDARY SOURCES AND RECOVERY

Gem stones recovered from jewelry are recut and set in jewelry of modern design. Pieces resulting from cutting fine gem stones are processed into gems of lower quality or are used for tumbled baroque gems.

RESERVES

The United States has no known large resources of precious gem stones. Occasional finds of diamond have been made but no great diamond pipes or alluvial deposits similar to those of Africa have been discovered.

Numerous domestic deposits of semiprecious gem stones are known and have been mined during the past decades. However, no systematic evaluations of the magnitude of these deposits has been done, and no positive statement can be made about them.

The world gem diamond reserve is estimated to be 100 million carats. Nearly all of this quantity is in Africa. Possible offshore underwater deposits have not been considered in making the estimate. Underwater deposits off the coast of southwest Africa being prospected will probably add to the world reserve estimate. Some production of gem diamond is reported in the U.S.S.R., but no information on reserves is available. World reserve data on other precious and semiprecious stones are lacking.

SOURCES OF STATISTICAL INFORMATION

The Bureau of Mines obtains domestic gem stone production and supplemental data from an annual canvass of all known major producers. The Bureau of the Census, U.S. Department of Commerce, collects data on imports, exports, and reexports of gem stones on a monthly basis.

PRODUCTION AND TRADE

In 1963, production came primarily from Oregon, California, Texas, Arizona, Wyoming, Nevada, Utah, and Washington. The estimated value of U.S. production was more than $1.4 million, compared with less than $250,000 in 1900. Table 3 gives the estimated value of gem stone output in the United States; table 4 shows world production of gem diamond by countries; and table 5 shows precious and semiprecious stones imported for consumption in the United States.

Imports of natural, uncut precious and semiprecious gem stone are duty free. Duty rates for cut but unset precious gem materials follow: Diamond under 0.5 carat, ruby, sapphire, and synthetic gem stone quality material, 8 percent ad valorem; diamond over 0.5 carat, and marcasites, 10 percent ad valorem; emeralds, 3 percent ad valorem; other precious stones, 5 percent ad valorem; and precious stone not otherwise provided for in any other import category, 15 percent ad valorem. Rock crystal (clear quartz crystal) is dutiable at 21 percent ad valorem.

TABLE 3.—*Estimated value of U.S. production of gem stones*

Year	Value (thousands)	Year	Value (thousands)
1954–58 (average)	$849	1961	$1,309
1959	1,184	1962	1,296
1960	1,188	1963	1,421

TABLE 4.—*World production of gem diamond*

[Thousand carats]

Country	1959	1960	1961	1962	1963
Africa:					
Angola	516	658	688	762	759
Central African Republic	40	30	41	80	121
Congo (Léopoldville)	655	413	405	256	296
Congo (Brazzaville)				158	341
Ghana	876	773	654	628	536
Guinea	200	447	490	140	22
Ivory Coast		80	219	102	63
Liberia	470	577	596	225	240
Sierra Leone	644	912	799	707	555
South Africa, Republic of:					
Pipe mines:					
Premier	323	309	360	425	522
De Beers group	562	717	953	883	921
Others	30	40	35	36	37
Alluvial mines	250	240	240	290	294
South-West Africa	841	885	816	800	1,076
Tanganyika	274	287	340	323	276
Other regions:					
Brazil	180	175	175	175	175
British Guiana	22	61	68	60	60
Venezuela	15	14	60	94	38
U.S.S.R., India, and others	5	60	80	201	241
World total	5,903	6,700	7,019	6,347	6,572

TABLE 5.—*Precious and semiprecious stones (exclusive of industrial diamond) imported for consumption in the United States*

[Thousand dollars]

Item	1954–58 average)	1959	1960	1961	1962	1963
Diamond:						
Rough or uncut (suitable for cutting into gem stones), duty free	$74,434	$94,283	$87,518	$114,670	$102,548	$129,870
Cut but unset, suitable for jewelry, dutiable	69,385	86,366	78,037	78,605	89,188	93,977
Emerald: Cut but not set, dutiable	1,267	2,450	1,463	2,090	2,798	2,081
Other precious and semiprecious stones:						
Rough or uncut, duty free	425	678	620	1,169	1,765	1,708
Cut but not set, dutiable	2,774	3,990	3,967	3,900	5,102	5,183
Imitation and synthetic, dutiable	11,650	11,053	6,305	5,306	4,248	4,913
Total	159,935	198,820	177,910	205,740	205,649	237,732

Source: Bureau of the Census.

PRICES

The price of a finished gem stone usually is determined by demand and by its beauty, durability, rarity, freedom from defects, and perfection of cutting. An additional factor in establishing the price of gem diamond is the control over output and prices exercised by the Diamond Corp., Ltd.

In 1963, the range of retail prices for gem diamond was 0.25 carat, $72 to $340; 0.5 carat, $220 to $600; 1 carat, $575 to $1,650; 2 carats, $1,380 to $5,000; 3 carats, $2,880 to $9,900. Table 6 gives average prices paid for gem diamond and emerald per carat by importers.

TABLE 6.—*Average prices per carat of gem diamond and emerald imported for consumption in the United States.*

	1954–58 (average)	1959	1960	1961	1962	1963
Diamond:						
Rough or uncut	$70.65	$59.74	$64.09	$50.42	$72.15	$74.23
Cut but unset	104.52	94.20	97.30	93.67	90.79	92.35
Emerald: Cut but unset	30.92	27.56	18.01	9.19	14.22	10.90

Various transparent minerals, such as andalusite, diopside, epidote, kyanite, and sphene, when cut command a retail value of $2 to $50 per carat. The actual value depends on the size and quality of the stone. Prices of opaque minerals range from $5 to $30 per stone in the 10- to 15-carat size range. Cut synthetic emerald, depending on quality, ranges from $20 to $100 for a 1-carat stone and from $25 to $150 for a 2-carat stone. Cut synthetic spinel runs from $8 to $20 per carat in the size range from 1 to 10 carats. Boules of synthetic sapphire, spinel, and ruby sell for under 10 cents per carat.

TAXES

A depletion allowance of 15 percent is granted on domestic and foreign gem stone production.

An excise tax of 10 percent is imposed by the Government on the retail sales value of set or unset gems. Many States have a general sales tax ranging from 1 to 3 percent in addition to the Federal tax. Some States assess personal property taxes each year on privately owned jewelry and gem stones.

RESEARCH

Research on the production of synthetic gem stones is done by Linde Air Products Co., a division of Union Carbide Corp.; Stuart Laboratories, Inc.; National Lead Co.; Chatham Research Laboratories; Bell Telephone Laboratories; and General Electric Co. One result of this research is the development of synthetic gems with colors not found in nature. The Diamond Research Laboratory at Johannesburg, Republic of South Africa, conducts basic and applied research on gem diamonds.

Research also is being conducted on determining the conditions necessary to synthesize pure silicates, on developing hydrothermal techniques for growing sapphire crystals, on the use of ultrasonic vibrations for drilling and cleaning precious stones, and on developing automatic polishing machines (*22*).

OUTLOOK

The demand for gem diamond, especially in the larger carat weights, can be expected to rise because of increasing personal income of the population of the United States and other industrialized countries. Because of the increasing demand for precious stones for both adornment and investment, prices will continue to increase. The development of new diamond resource areas and the reactivation of older mine properties will assist the industry in meeting current and future demands.

The semiprecious gem requirements of the United States will continue to be met by the efforts of individual domestic gem stone collectors and mineral clubs along with imports of these materials from other nations The devel opment of commercial domestic semiprecious gem stone lapidaries and cutters will remain minimal owing to the high labor costs and relatively low value of the finished materials. However, gem and mineral collecting, cutting, and polishing will continue as a very popular hobby with a large segment of the population.

The demand for synthetic gem materials will continue to increase. Synthetic gem stone will find increasing use for mounted jewelry, and industrial demands will create new uses for these synthetics. Synthetic materials such as quartz crystal, ruby, and sapphire have been successfully used in industrial applications.

PROBLEMS

The lack of known domestic gem stone deposits and reserves that can be economically exploited remains the primary problem associated with this commodity.

Basic gem stone production statistics are difficult to obtain owing to the large number of unknown individual collectors. Because of this situation, no reliable estimate of gem stone production is available.

The development of a larger cutting and polishing industry is hampered by deficiency of well-developed gem deposits.

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GERMANIUM

By Donald E. Moulds [1]

GERMANIUM is produced commercially as a byproduct in mining and refining ores of other metals. The major domestic source of germanium has been the Tri-State zinc district of Missouri-Kansas-Oklahoma and the Illinois-Kentucky fluorspar district. The Tsumeb mine in South-West Africa and the Prince Leopold mine in the Congo (Léopoldville) are the major sources of free world supply. Fume and residues from base metal refining and coal ash from coal-burning operations contribute small amounts.

Industrial organizations engaged in producing and refining germanium are also few, but the capacity of the industry is ample to assure a continuing supply well able to meet foreseeable demand. Companies engaged in manufacturing semiconductor components are relatively numerous and widely scattered in the United States and foreign industrial areas.

The only significant industrial use for germanium is as a semiconductor component for electronic and electrical devices. The rapidly expanding use of these devices in the field of communications, power transmission, data processing, missile guidance, and astronautics has been accompanied by major advances in component manufacturing techniques and utilization; these advances have significantly slowed the rate of consumption of germanium per component.

The vulnerability of germanium to substitution by other semiconductors with comparable performance characteristics in the highly competitive electronics industry necessitates a continuing emphasis on germanium research both in the semiconductor field and in other potential applications. In addition an ample supply must be maintained at a competitive price.

BACKGROUND

In 1871 Mendeleef, a Russian scientist, predicted the existence of an element, eka-silicon, occupying number 32 in the periodic table. Fifteen years later, Clemens Winkler, a German scientist, isolated the element from the mineral argyrodite and named it germanium in honor of his native country. Investigation of the properties of germanium confirmed the predictions of Mendeleef (*6*).[2]

Germanium remained little more than a scientific curiosity until the early 1920's when extensive studies were conducted on possible applications of the substance. In 1922 the therapeutic value of germanium oxide in treating anemia was reported. The first commercial producer of germanium dioxide was the Otavi Company in Frankfurt, Germany, in 1930. The source of the material was germanite ore obtained from the Tsumeb mine in the then-German colony of South-West Africa.

The zinc ores of the Kansas-Missouri-Oklahoma area contain a small amount of germanium which constitutes an impurity in refined zinc and had to be removed by a difficult and costly process. The Eagle-Picher Co. initiated a research program to determine what, if any, commercial application could be developed for this byproduct. Fundamental research programs at Bell Telephone Laboratories and Purdue University developed the semiconductor application for germanium and by 1941 a germanium-recovery facility was in operation in connection with the Henryetta, Okla., zinc smelter of The Eagle-Picher Co.

The semiconductor properties of germanium were first utilized extensively for crystal diode rectifiers during World War II. In 1948 the germanium transistor was developed, and expanded research and availability of high-purity germanium has revolutionized the communications industry. The semiconductor devices currently utilized—diodes, transistors, and rectifiers—have permitted miniaturization of radios,

[1] Commodity specialist.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

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television, hearing aids, and telephone dialing equipment and have allowed major advances in astronautics, missile guidance, and worldwide communications.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Shipments of germanium semiconductor devices in the United States in 1963 approached 550 million units valued at $209 million. Some 130 plants are engaged in manufacturing the specialized germanium diodes, rectifiers, and transistors required in a wide scope of electrical equipment.

The U.S. producers of germanium from domestic and foreign source material are American Metal Climax, Inc., Carteret, N.J.; American Zinc Company of Illinois, Fairmont, Ill.; The Eagle-Picher Co., Henryetta, Okla.; and Sylvania Electric Products, Inc., Towanda, Pa. In addition, United Minerals and Chemical Corp., New Brunswick, N.J., and Penn Rare Metals, Revere, Pa., a division of Kawecki Chemical Co., produce germanium from scrap processing. The three major representatives of foreign germanium producers marketing imported metal and dioxide in the United States are The African Metals Corp., American Metal Climax, Inc., and Harmon Lichtenstein and Co., all with offices in New York City.

The Tri-State zinc-lead mining district of Kansas, Missouri, and Oklahoma has been the major source of the domestic production of germanium since The Eagle-Picher Co. started commercial production in 1941. Zinc concentrate from the Illinois-Kentucky fluorspar district is treated at Fairmont, Ill., for recovery of germanium.

The Tsumeb Corp., Ltd. produces germanium from the copper-lead-zinc ores of the Tsumeb mine in South-West Africa by selective flotation and refining to germanium dioxide. The dioxide is further processed to metal at the Carteret, N.J. plant of American Metal Climax, Inc.

Union Minière du Haut-Katanga produces germanium from the copper-zinc ores of the Katanga area of the Congo (Léopoldville). The germanium is contained in concentrates collected from the fume and dusts resulting from copper smelting and shipped to Belgium for refining. Union Minière operates the largest germanium refinery in the world at Olen, near Antwerp, Belgium, through its affiliate the Société Générale Metallurgique de Hoboken. The capacity of the plant is 135,000 pounds of electronic-grade germanium dioxide per year (65 percent germanium).

The Société de la Vieille Montagne has produced germanium at Balen, Belgium, since 1952 as a byproduct of its zinc-refining operations. In the United Kingdom, Johnson, Matthey and Co. began producing germanium in 1950 from coal flue dust obtained at its producer-gas plant. The zinc plant of Montevecchio near Venice, Italy, produces a small quantity of germanium from zinc-refining operations. West Germany and Japan also are producers of germanium from zinc concentrates, coal dusts, refinery residues and other source materials. Little is known of the germanium industry of the U.S.S.R., but the wide use of semiconductors and extensive published research data indicate a major output from the complex ores of the Kazakhstan area.

DEFINITIONS OF TERMS, GRADES, AND SPECIFICATIONS

Germanium is metallic-looking but displays the physical and chemical properties of a metal only under special conditions. It is a semiconductor with properties ranging between those of a metal and of an insulator. Structurally, germanium has the cubic symmetry of the diamond crystal lattice and four valence electrons. Some of the more distinctive properties of germanium follow (*5*):

Atomic weight	72.60
Density at 25° C, g/cm³	5.32
Melting point, °C	940
Boiling point, °C	2,700
Band gap at 0° K, electron-volts	0.75
Intrinsic resistivity at 27° C, ohm-cm³	47
Electron mobility, drift, cm²/volt/sec	3,800
Hole mobility, drift, cm²/volt/sec	1,800
Debye temperature, °K	362
Thermal conductivity, cal/sec/cm²/°C	0.15
Dielectric constant	15.7
Specific heat at 25° C, val/g/°C	0.074
Bulk rigidity modulus, dyne/cm²	1.3×10^{12}
Thermal expansion coefficient (linear) at 25 °C per °C	6.1×10^{-6}
Latent heat of fusion, cal/mol	8,300

Germanium is available in three forms: as reduced ingots, purified ingots, and single crystals. Standard ingots are 15 to 17 inches long and weigh approximately 1,750 grams. Mono, or single, crystals grown are supplied in sizes up to 3 inches in diameter and weights up to 2,000 grams. These crystals are normally grown in the 1:1:1 orientation.

The standard measurement of purity of electronic-grade germanium is resistivity. These measurements are made using a four-point probe on an abraded surface at 25° C. In the polycrystalline form, measurements are made along the bottom of the ingot.

Specifications for marketable electronic-grade germanium have changed as the requirements of the electronic industry became more rigid. It

is typical for germanium to be offered to consumers under the following minimum resistivity specifications:

As-reduced	5 ohm cm minimum.
Purified	40 ohm cm minimum.
Monocrystalline	40 ohm cm minimum.

Germanium is also offered commercially in the form of monoxide, as dioxide, and compounded with other metallic and nonmetallic substances.

Test procedures for determination of volatile content and bulk density of germanium dioxide have been accepted by the American Society for Testing and Materials (*2*).

TECHNOLOGY

Germanium is obtained commercially as a byproduct of zinc production and from germanium-bearing minerals as a coproduct of base-metal refining (*3*).

Geology

There are no native occurrences of germanium, and its abundance in the earth's crust is 1 part in 150,000 or 6.7 parts per million. The more important germanium minerals follow. Germanite, $7CuS \cdot FeS \cdot GeS_2$, is a complex mineral found mainly at Tsumeb, South-West Africa, in isolated pockets in the main copper-lead-zinc ore body. Its average germanium content is 5 percent. Argyrodite, $4\ Ag_2S \cdot GeS_2$, from which Winkler first isolated germanium, occurs at the Himmelfurst and other mines at Freiberg, Saxony, and at Aullagus, Bolivia. Its germanium content is between 5 and 7 percent. Canfieldite and ultrabasite are also found at these localities. The former contains 1.8 to 6.5 percent germanium and the latter contains 2.2 percent. Renierite, $(Cu,Fe)_3(Fe,Ge,Zn,Sn)S,As)_4$, is found mainly at the Prince Leopold mine at Kipushi, the Congo (Léopoldville), and at the Tsumeb mine in South-West Africa. The germanium content ranges from 6.37 to 7.80 percent.

The most common occurrence of germanium is in minute quantities within the molecular structure of other minerals. It occurs most abundantly in sphalerite (ZnS) in quantities ranging from traces to tenths of 1 percent. Cinnabar sometimes contains germanium in tenths of 1 percent and enargite up to 0.1 percent. Pyrargyrite from the silver mines of Bolivia contains up to 0.1 percent, and some tin-bearing sulfides contain 0.5 percent. Germanium has also been said to occur in calamine, pyrites, euxenite, cassiterite, and tantalum and columbium ores. However, the amounts recorded are small, usually about 0.001 percent or less.

From the extensive studies made on the germanium content of coal it is possible to set down some broad generalizations on the subject:

1. Coals with a high vitrain (woody coal) content are much richer in germanium than coal with a low vitrain content.
2. Low-ash coals are richer in germanium than coals with a high ash content.
3. Geologically older coals usually have a lower germanium content than more recent coals.
4. Germanium is believed to be associated with the organic matter and not the mineral matter in coal.
5. The germanium is usually concentrated in the top or bottom few inches of coal beds.

Techniques used for the analysis and detection of germanium are discussed in detail in germanium literature concerning its occurrence in coals (*1, 4, 9*). The semiquantitative spectrographic method provides the most rapid means of obtaining information on the magnitude of germanium concentration. For more precise estimates of germanium concentration the quantitative spectrographic method provides a sensitive, rapid, and reliable technique. Analytical chemistry of germanium by wet methods is based on the separation of germanium from most interfering elements by distillation as volatile germanium chloride. Then the germanium is determined in the distillate by analytical methods that include gravimetric, volumetric, or colorimetric procedures. The spectrophotometric method of Cluley (*1*), which utilizes phenylfluorenone, is widely used. The spectrophotometric procedure is more sensitive than the quantitative spectrographic method, but it requires more involved and time-consuming sample preparation.

In the metallugical recovery of germanium from the source materials, various processes are used to obtain a product suitable for recovery of the germanium as a crude tetrachloride. The subsequent process of refining is quite similar for all production plants.

Metallurgy

In the metallurgical recovery of germanium from Tri-State zinc sulfide concentrate, the sulfur is first removed by roasting, and the zinc germanium, and cadmium are converted to oxides. The oxides are given a chloridizing roast to convert cadmium and germanium to chlorides which are volatilized. These are condensed and collected electrostatically to yield a

product from which germanium can be distilled as the tetrachloride.

Zinc ores from the Illinois-Kentucky district are concentrated and sintered in the same manner as the Tri-State ores. The germanium reports in the byproduct fume which is leached with sulfuric acid to dissolve zinc and cadmium and leave a sludge containing germanium. Germanium is then dissolved by hot, strong sulfuric acid and precipitated with hydrogen sulfide. The sulfide precipitate is roasted and the germanium oxide is reacted with strong hydrochloric acid to form germanium tetrachloride.

The copper-zinc ores of Katanga contain germanium as the mineral renierite. In selective flotation of the ores, the renierite reports with the copper concentrate. Part of the renierite is then recovered by magnetic separation. This product is treated in an electric furnace to obtain a fume containing germanium dioxide. Germanium-bearing fume and dust are also recovered from the copper smelting. They are then baked with sulfuric acid and leached to obtain a germanium-bearing solution from which, after oxidation, the germanium is precipitated with magnesia and copper hydrate to form a concentrate which is then shipped to Belgium for further refining.

Flue dusts are smelted with soda ash, lime, copper oxide, and coal dust to form a regulus and slag. The regulus, containing germanium, is reacted with chloride under a dilute solution of ferric chloride, and the crude germanium tetrachloride is distilled. Arsenic chloride accompanying the germanium is eliminated by refluxing with copper turnings.

Controlled purity is essential in germanium for electronic uses. Less than 1 part per 100 billion of some impurities has an observable effect. Germanium tetrachloride is purified by distilling it from strong hydrochloric acid solution. After distillation it is hydrolyzed in ice water to obtain pure germanium dioxide, which is washed completely free of chloride and is then ready for reduction to the metal.

Germanium dioxide is reduced by heating in hydrogen. The dioxide is packed in graphite boats and heated to 650° C in an electric furnace in a current of hydrogen until no more water is evolved. The hydrogen is then replaced by helium or nitrogen, and the temperature is raised to 1,000° C to melt the resulting powder.

When germanium is used as a semiconductor, it is necessary to have an ultra-high purity which is measurable in parts per billion and which is achieved by zone refining. A germanium ingot 12 to 20 inches in length and 1 to 1½ inches in diameter is passed through a series of induction-coil heaters, each of which produces a molten zone. Relatively pure germanium crystallizes at the trailing edge of each molten zone, and impurities remain in the molton zone and are gradually isolated toward one end as the bar moves through the heaters. After the desirable number of passes are made through the induction stages, the end of the ingot containing the impurities is cut off.

The ultrapure germanium ingot thus produced is polycrystalline, and for semiconductor use it must be in the form of a single crystal. Two methods of single-crystal growth were developed for growing germanium crystals. The first, originated by Czochralski, is called the vertical pulling method. A crystallographically oriented seed-crystal is dipped into molten germanium in a graphite crucible and slowly withdrawn. Then, by adjusting the heat input and heat losses, and under proper conditions and synchronization, the germanium will grow on the seed and extend its crystal lattice until the charge has been converted to one crystal.

The second method, called the horizontal or zone-leveling technique, is a modification of zone melting. The crystal seed is placed at one end of a horizontal, carbon-coated silica crucible filled with ultrapure polycrystalline germanium. The whole may be converted into a single crystal with the controlled addition of a desired impurity by carefully moving a molten zone toward the seed, melting into it, and then slowly withdrawing the molten zone.

USES

The major use of germanium is in manufacture of semiconductor devices. The advantages of these devices—extremely small size and weight, small current consumption and immediate availability of operation, and long operating life, ruggedness, and mechanical stability—have resulted in a wide range of application in the field of communications, power rectification, data processing, astronautics, and missile guidance.

Germanium has a potential use in the production of glass with special properties. Glass in which all or part of the silicon dioxide has been replaced by germanium dioxide displays an unusually high index of refraction and is useful for wide-angle camera lenses and microscope objectives. Glass containing magnesium germanate can transmit infrared radiation over broad regions of the spectrum and is used in infrared spectroscopes and other infrared optical instruments. Germanium-magnesium phosphors have been used in fluorescent lights.

Germanium gives increased hardless and strength to copper, aluminum, and magnesium and improves their rolling properties. Ger-

manium-gold alloys have been experimented with as dental alloys. The alloys of the germanium-gold series can be used as precision castings since they expand on cooling. The addition of small percentages of germanium to gold sharply reduces the melting point, and the 12-percent germanium eutectic has a melting point of 356° C. This may be used to advantage as a gold solder and in jewelry manufacture, because the gold color remains.

Germanium is beneficial as a storage battery solution additive in producing more usuable ampere-hours, especially in intermittent-use lead-acid batteries. Transistorized automobile ignition systems are currently in the demonstration stage (*5*).

BYPRODUCTS AND ALTERNATE MATERIALS

Germanium is a byproduct closely associated with base metals and dependent upon these metals to bear the major share of the cost of extraction and processing. The predominate use of germanium as a semiconductor incorporates a vulnerability to direct substitution by other semiconductors with comparable performance characteristics such as high-purity silicon and certain tellurium, selenium, indium, and gallium bimetallics.

Germanium diodes, transistors, and rectifiers have replaced the vacuum tube or electron tube in many applications where cost-performance ratios have been competitive.

SECONDARY SOURCES

The germanium secondary metal market is currently negligible; there is some small-scale salvage and marketing of obsolete devices. New scrap generated in manufacture of semiconductor devices such as cuttings, grindings, and rejections is usually returned to the germanium producers for reprocessing on a toll basis. Currently reprocessed scrap represents up to 60 percent of that shipped to manufacturers.

RESERVES

The known occurrences of mineral deposits valued chiefly for germanium are of small significance and none are presently utilized for recovery of germanium. The small percentage of germanium (0.01 to 0.1 percent) associated with ores of zinc and other base metals is economically recoverable only because in the process of refining the host metals the germanium is concentrated in byproducts to a degree susceptible to recovery and refining at an acceptable cost.

Variation in content of ores and recovery of germanium is not presently known to the degree necessary for compilation of world resources. The byproduct relationship of germanium to base-metal ores in the Congo (Léopoldville), South-West Africa, and the United States indicates, however, that the potential is adequate to meet any foreseen demand.

A relatively large potential source of germanium is the germanium compounds found in amounts ranging from 1 to 4 percent in certain coal ashes and flue dusts. It has been estimated that in the United Kingdom alone 2,000 tons of germanium yearly may be present in stack gases, flue dusts, and ashes at plants burning germaniumiferous coal.

Coal deposits in the United States have been extensively studied (*9*). Data on germanium content of coals in West Virginia, Illinois, and Kansas has been reported (*1*) and a large potential supply exists in certain coals containing 0.05 to 0.1 percent germanium in the ash. Research on extraction is well advanced toward an economic method of commercial production in event of a substantial increase in demand.

SOURCES OF STATISTICAL INFORMATION

Statistical information on germanium production and consumption is inadequate to provide an accurate industrial survey. Information available is published in the "Minor Metals" chapter of the Bureau of Mines Minerals Yearbook. The Business and Defense Administration of the U.S. Department of Commerce publishes quarterly reports on shipments and value of electrical components including those incorporating germanium. The Bureau of the Census, U.S. Department of Commerce, provides statistics on imports of germanium in concentrates and as dioxide and metal.

PRODUCTION, CONSUMPTION, AND TRADE

Germanium production has increased rapidly since 1948, and free world shipments were well over 200,000 pounds in 1962 including scrap returned for reprocessing and reshipment as well as primary material. The increased production along with significant advances in manufacturing efficiencies has resulted in an excess of domestic and foreign production capacity.

In 1963 an estimated 20,000 pounds of primary germanium was consumed in the United States, with total consumption of primary plus reprocessed scrap about 45,000 pounds. The number of semiconductor devices using germanium has shown a remarkable growth in re-

cent years. U.S. factory shipments of semiconductor devices using germanium advanced from 218 million units in 1960 to 547 million during 1963. Value, however, declined from $254 million in 1960 to $209 million in 1963. The increased efficiency of utilization and manufacture as well as price reductions for germanium metal are indicated in the greatly reduced unit value.

U.S. production of primary germanium has been augmented by imports of germanium in base metal concentrates from South-West Africa as well as germanium concentrates for refining. Imports of germanium metal and germanium dioxide, principally from Belgium and West Germany, amounted to 30,748 pounds valued at almost $2 million in 1961 but declined to 5,000 pounds valued at $284,000 during 1963.

The rate of duty effective under the revised tariff schedule of August 31, 1963, and the General Agreement on Tariffs and Trade is 10.5 percent ad valorum for germanium as dioxide and as unwrought metal.

PRICES

Price quotation for germanium ingots or cut ingots is normally based on the metric system of grams and kilograms. The most generally accepted standard measurement of purity and price basing is resistivity, made by using a two- or four-point probe on an abraded surface at 25° C. Polycrystalline ingot germanium, as reduced, has a resistivity in the range of 5 ohms per centimeter (minimum). This quality was quoted at 25.20 cents per gram in 10-kilogram lots, delivered to buyers' works, at the close of 1963. Intrinsic or ultra-high-purity polycrystalline germanium (minimum resistance of 40 ohms per centimeter) was priced slightly higher. Single-crystal germanium was quoted at 56 cents per gram, approximately twice the price of polycrystalline material. High-purity germanium dioxide (65 percent GeO_2) was quoted at 15.1 cents per gram approximately one-half the price of polycrystalline metal.

TAXES

The depletion allowance for germanium is 15 percent, domestic and foreign.

RESEARCH

Large-scale research on germanium was focused first on removing the element from zinc concentrates and later on the development of a process for refining the extracted germanium on a commercial basis. When this had been accomplished, the attention of the research program was directed toward finding industrial applications for the metal.

The search for significant industrial applications was successful in introducing the germanium diode during World War II. The transistor developed in 1948 by W. Shockley, J. Bardeen, and W. Brattain at the Bell Telephone Laboratory provided a major advance for germanium. These men received the Nobel Prize for their significant contribution to knowledge of solid-state physics which revolutionized electronic theory and design.

Intensive research conducted on the commercial recovery of germanium from coals and other hydrocarbons has not yet resulted in a competitive process. The large potential existing in this area, however, continues to provide an incentive for continued research (*7*, *8*, *10*).

A Germanium Research Committee was formed in 1959 by six domestic and foreign producers. The purpose of this group is to unite their research efforts to develop new uses for germanium and to disseminate information on germanium and its applications. Research being sponsored by the group is conducted by many research organizations throughout the world (*5*).

OUTLOOK

Semiconductor devices will continue to be the predominant use of germanium. There is a possibility that germanium in these devices may be replaced by materials that are less costly or more efficient or that have better thermal stability. Various alternate materials, principally silicon, have been developed, but for the most part they have found specialized or new applications rather than displacing germanium.

Although use of semiconductors is expected to increase substantially, germanium consumption will rise only moderately owing to the increasing efficiency of manufacture and utilization and some replacement by alternate materials.

The ready availability of germanium has spurred research in other applications such as specialized optical equipment, gages, precision casting alloys, storage battery electrolytes, and chemical catalysts. Significant promise for some applications could result in greater diversification and consumption. Germanium consumption in the United States in all uses could double from the estimated 20,000 pounds of new production in 1963 to 50,000 pounds within the next 10 years, and the free world demand, prin-

cipally in Japan, West Germany, and the United States, could increase some 50 percent to 150,000 pounds annually.

The world supply of germanium metal and compounds should be ample to meet foreseeable demand in current industrial applications for the next 10 years, provided the African countries that constitute the major free world source are politically and economically stable. Primary germanium for domestic use will be supplied by domestic zinc smelter fume, imported concentrates, refined metal, and compounds. It is unlikely that recovery of germanium from domestic zinc-mining operations will rise, therefore, any increase in requirements will be met by imports originating at central and south African base-metal mines.

Flue dusts and residues from metallurgical operations other than zinc plants and coal ash derived from plants burning high-germanium coals are potential domestic sources, but it is doubtful that competitive commercial methods will be developed in the near future under the anticipated level of demand.

PROBLEMS

The major problem facing the germanium industry is the lack of diversified industrial application for the element. While the semiconductor industry has provided the incentive for past research and production expansion, the future of germanium in this industry is uncertain. Research must be emphasized to overcome certain problems existing in manufacture, to develop new and diverse applications that will utilize significant quantities, and to assist in industrial adaptation of research findings.

Domestic germanium output is dependent upon zinc production. Coals and flue dusts of other metallurgical operations have not been utilized as sources of germanium because of problems concerning methods of economic recovery and evaluation of potential source material and future markets.

The lack of comprehensive resource information and statistical data pertaining to world production, shipments, consumption, and stocks of germanium is a handicap in the evaluation of the industry.

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GOLD

By J. Patrick Ryan [1]

GOLD was one of the first metals used by man and has been prized because of its beauty, scarcity, and imperishability. Because of these qualities it has been widely used as a medium of exchange and a measure of value in world commerce. The use of gold in the arts and industries has increased in recent years as its special properties have led to applications in modern science and technology.

Total world production of gold from 1493 to 1963 is estimated at 2,216 million troy ounces, about 14 percent of which was produced in the United States. The United States was the leading gold producer of the world from 1849, the year after gold was discovered in California, until 1905, and in recent years has ranked fourth after the Republic of South Africa, Canada, and the U.S.S.R. The estimated world production of gold in 1963, 44.3 million ounces, was valued at $1,550 million—an alltime record.

Governments and central banks use most of the world's gold production to provide monetary stability for paper currencies and to settle international trade balances. A moderate quantity of gold is used in the arts and industry, and a substantial part of gold production is hoarded and held as an investment. At the end of 1963, the estimated free world monetary gold reserve was $42,285 million, about 37 percent of which was held by the United States.

The official U.S. price of gold has been $35 per ounce since 1934.

The reserve of gold-bearing ores in the United States was estimated at 20 million ounces in 1963, less than one-third of the 1944 reserve. This reserve is adequate to maintain output near the 1963 level for several years at current price-cost conditions. Consumption of gold has increased in recent years, especially in industrial and defense applications; in 1963 nearly 3 million ounces, or about twice domestic production, was used in the arts and industries of the United States. The deficit in new supply was balanced by withdrawals from the Treasury reserve.

BACKGROUND

Early methods of mining gold were primitive and production was small. World output increased rapidly after 1700 as deposits in the U.S.S.R. and South America were more extensively exploited and new deposits were discovered and developed in North America. The Southern Appalachian States began to produce gold in the early 1800's, but the output furnished only a small part of the world gold supply. After the discovery of gold placers in California (1848) and later deposits elsewhere, the United States became the leading world gold producer for more than half a century (*14*).[2]

Since 1905 the Republic of South Africa has been the leading gold-producing country. Three nations have ranked second, the United States (until 1930), Canada, and (probably) the U.S.S.R. (after 1934). Despite an increasing yield of byproduct gold from base-metal mining, the trend in domestic gold production was generally downward after 1915, recovering strongly after the price of gold was raised from $20.67 an ounce to $35 in 1934. Production reached an alltime high in 1940, dropped sharply during World War II, and had risen to one-half the prewar output by 1950. Since 1950 gold production has declined, and in 1963 it reached the lowest peacetime level in more than 100 years.

[1] Commodity specialist.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

In 1963 domestic production of gold was 1.45 million ounces, of which 13 percent was recovered by placer mining, 51 percent from gold and gold-silver ores, and 36 percent as a byproduct of base-metal ore. About 1,063 lode and placer mines were active and employed approximately 5,200 persons. The bulk of byproduct gold came from large-tonnage copper mines treating low-grade ore.

In 1963 of the 25 leading U.S. gold producers, 4 were lode gold mines, 5 were placers worked by bucketline dredges, 10 were copper mines, 3 were lead-zinc mines, 2 were copper-lead-zinc mines, and 1 was a zinc mine. These mines supplied about 94 percent of the domestic output valued at $50.9 million.

Gold is found in some quantity in nearly every country. In recent years gold has been produced in 75 countries. In the United States gold has been mined in 25 States, the principal ones in order of total recorded output being California, Colorado, South Dakota, Alaska, Nevada, Montana, and Utah. In order of current production they are South Dakota, Utah, Arizona, Alaska, Nevada, Washington, California, and Colorado. Current output from Utah and Arizona is almost entirely as a byproduct of base-metal ores.

The Republic of South Africa, the leading gold-producing country since 1905, supplied about 53 percent of world output in 1963. The U.S.S.R. probably has been second in gold production since 1934; Canada ranks third, supplying about 8 percent; and the United States is fourth, furnishing about 3 percent of the world output.

With few exceptions, domestic lode gold deposits are relatively small, widely scattered, and low grade. The Homestake mine in Lawrence County, S. Dak., the Nation's leading gold producer, treated about 1.9 million tons of ore in 1963—about 5,200 tons per day, by amalgamation and cyanidation. The Utah Copper mine at Bingham, Utah, the second largest gold producer, recovers gold as a byproduct of treating copper ore; about 26 million tons of ore, containing about 35 cents per ton in gold, was treated at this mine in 1963. These two mines produced nearly 57 percent of the total domestic output of gold in 1963. Nearly all of the U.S. placer mine production currently comes from Alaska and California and is recovered chiefly by bucketline dredging. In 1963, bucketline dredges treated 18.4 million cubic yards of gravel, averaging 31 cents per cubic yard in recoverable gold.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

According to the classification of ores adopted on the basis of smelter terminology, smelter settlement contracts, and metal recovery, gold, gold-silver, and silver ores with the base metal content too small to be classified as either copper, lead, or zinc ores are classified as dry ore regardless of the ratio of concentration. The dry ores are chiefly siliceous, valuable for their silver and gold content and in some instances for their fluxing properties, regardless of method of treatment. Dry gold ores are defined as those in which the gold value equals or exceeds three-fourths of the combined gold and silver values; dry silver ores are those in which the silver value equals or exceeds three-fourths of the combined gold and silver values. Dry gold-silver ores are defined as those in which both the gold and silver values equal or exceed one-fourth of the combined gold and silver values. Tailings and slags follow the same scheme of classification as ores.

The classifications are not to be modified by considerations of payments of metals by smelters or custom mills or by method of treatment by the smelters. Payments for gold are made on the basis of the troy ounce, 1,000 fine, at the official U.S. Treasury price of $35 per ounce.

The troy ounce, the basic unit of measuring gold and silver, may be defined as equivalent to 20 pennyweight or 480 grains. It is about 10 percent heavier than the common avoirdupois ounce. There are 14.583 ounces troy in an avoirdupois pound. It has become almost universal practice to weigh gold in troy ounces and decimal parts of an ounce or in pennyweights (dwts.) and decimal parts of a dwt. Fineness defines the proportion of pure gold in bullion or coin expressed in parts per thousand. Thus, fine gold is 100 percent pure, 1000/1000 fine. U.S. gold or silver coin is nine-tenths or 900 fine.

The term "karat" means a 24th part and is used to express the weight proportion of fine gold in an alloy; thus, pure gold is 24 kt; 18 kt alloy contains 18/24 or 75 percent gold. U.S. regulations require that a karat gold article of jewelry must be at least 10 karat or 416 fine. A tolerance of one-half karat is permissible. "Rolled gold plate" or "gold filled" are terms referring to articles made of base metal on which karat gold has been joined by soldering, brazing, or mechanical means.

Karat golds are made in red, yellow, green, and white as standard colors. The colored golds are basically ternary alloys of gold, silver, and copper. Zinc and nickel are also added to some jewelry karat golds. White golds are generally

composed of gold, copper, zinc, and nickel. Yellow golds are generally alloys of gold and copper containing some silver and zinc. Green gold is chiefly gold and silver containing some copper and very little zinc.

TECHNOLOGY

Geology

Gold deposits are found in many types of rock and in formations of all geological ages, but most of the productive deposits are associated with rocks of very early or of comparatively recent age. Nearly all gold-bearing deposits occur near acidic igneous intrusions, with which they show genetic relationship (*5*). The general deposit types include magmatic, contact metamorphic, replacement (lode, massive, and disseminated), and cavity filling (fissures, stockwork, saddle reef, breccia, and conglomerates). Gold, associated base metals, and gangue minerals occur in primary deposits in many combinations. Weathering and erosion cause gold in the free or metallic form to be released from primary deposits and to accumulate as nuggets and grains, forming residual or stream placers. Although the richest lode gold deposits have probably been found in small fissure veins with predominant quartz gangue, much larger quantities of gold have been mined from large, moderate-to-low-grade deposits.

Lode Mining

Methods of mining gold ore vary considerably from one mine to another and are based principally on such factors as size and shape of the ore bodies, physical and mineralogical character of the ore and surrounding rock, and depth of mining. The overall objective is to extract the maximum quantity of ore at the lowest cost consistent with safety.

The Homestake, the only large gold mine operating in the United States, is being mined through 3 operating shafts on some 30 levels, from the 1,400- to the 6,200-foot level. More than 200 miles of development workings consisting of drifts and crosscuts have been driven to provide access between shafts and ore bodies and to reveal the location and form of the ore bodies on successive levels. Shrinkage stoping, with square-set stoping of pillars, used for many years at Homestake to remove ore between levels, has been almost entirely superseded in recent years by open cut-and-fill stoping, as the mine became deeper and rock pressures increased. At present cut-and-fill stoping is providing better ore extraction and has proved safer and less expensive than other stoping methods. Crosscuts 7 by 7 feet in cross section are driven from development drifts at 200-foot intervals; raises 5 by 7 feet in cross section are driven from the crosscuts through the ore to the level above; and mining is begun in the raises at the bottom of the ore. A cut 18 feet high is mined as far out from the raise as the ore extends, and the broken ore is slushed into the raise, loaded into cars, and transported to the surface. When a stoping cycle is completed the two-compartment chimney, which is built into the raise, is carried to within 7 feet of the stope back, and the open stope is then filled with sand to the top of the chimney. After the plank floor is laid on the fill, the stope is ready for mining again. When the stope is mined up to the next level and breaks through into the crosscut, it is mined up 18 feet above the track level. A timberline is installed on top of the sand and covered with sand; it then serves as a haulageway for removing the ore up to the next level. The length that a cut-and-fill stope can be mined depends on the width of the ore body. Some stopes that are not over 60 feet in width have been mined 400 feet in length.

Milling and Treatment

Lode gold is recovered by cyanidation, amalgamation, flotation, gravity concentration, and smelting or by a combination of these processes. Metallurgical recoveries are high, sometimes exceeding 95 percent (*4*). Some mills recover a gravity or flotation concentrate that is treated by amalgamation and/or cyanidation, sometimes preceded by roasting. The concentrate may be shipped to a custom mill or base metal smelter, thus saving outlay for plant. All types of gold ore may be treated by direct smelting. Smelters may pay for siliceous or basic ingredients for their fluxing qualities.

Some of the early gravity concentrating devices used to recover gold, including blanket strakes, various shaking tables, and jigs, are still used at some plants. In the past 20 years the fundamentals of gold-mining practice and types of equipment used have changed little, but machine design and techniques have been greatly improved. Outstanding developments have been principally in crushing, grinding, and classifying; in applying flotation to certain ores; and in improving precipitation and roasting techniques. The adoption of hydrocyclones for classifying, thickening, and concentrating; fluid-bed roasting; and carbon cyanidation has increased operating efficiency and lowered costs.

At the ore-treatment plants of the Homestake Mining Co., approximately 70 percent

of the gold is recovered by amalgamation and 27 percent by cyanidation. The crushed ore from the gyratory crushers is reduced to about 70 percent through 200-mesh by two-stage grinding, using rod mills in open circuit and ball mills in closed circuit with rake classifiers. One grinding circuit uses a ball mill and cyclones. The pulp from the ball mills passes over amalgamators, which recover the major part of the gold in the form of amalgam. Rake classifier overflow is separated into sands and slimes in bowl classifiers and treated by cyanidation in separate sand and slime leaching plants. Sand leaching in vats by gravity percolation recovers about 18 percent of the gold produced. Slime leaching under pressure in filter presses recovers about 9 percent of the total gold. The gold in the cyanide solutions is recovered in the precipitation units by adding zinc dust, and the resulting precipitate is smelted to produce crude bullion. The amalgam is retorted in retort furnaces; the gold residue remaining and the crude bullion from the precipitate are melted and treated by chlorination; and the refined product is poured into 35-pound gold bars.

Several machines and techniques first used by the gold-mining industry have found widespread use in treating other ores. Agitation by mechanical and compressed air methods, slime thickening and washing, and continuous vacuum filtration have been adopted by many industries that handle finely divided solids in liquids—sewage treatment, water purification, and many wet chemical processes.

Placer Mining

Gold placer-mining comprises the work of excavating and delivering auriferous gravel to a washing plant for recovering the gold it contains (*1*, *7*, *8*, *9*). Placer gravel is excavated and fed to the washing plant by small-scale hand methods and by mechanical or hydraulic equipment. Gravel deposits, particularly those not adapted to bucketline dredging, are mined with dragline excavators and treated in nearby washing plants. Buried placers, too deep for stripping, are mined underground. Gold is recovered as a byproduct at several plants that produce building sand and gravel from streams. Floating dredges, combining the digging, washing, and tailings-disposal plants in one self-contained unit, handle 12,000 cubic yards or more of gravel a day.

Placer-mining recovery methods are based largely on gravity concentration and amalgamation. The basic device usually employed is some form of sluice, over which a stream of water washes the gravel. Mercury is often placed in the riffles. Undercurrents are sometimes employed in wide sluices through which very fine gold particles may pass to an undersection; matting, carpet, corduroy, or small-size riffles catch the gold. Jigs may supplement or be used in place of tables. Gold is recovered from the heavy sand concentrate in amalgamating barrels. Recovery of coarse and moderately fine gold may exceed 90 percent, but that of fine or "flour" gold is low, particularly when clay is present in quantity.

Dry placer concentration processes, using air pulsations instead of water, have been developed in some areas in the Southwest (*7*).

Byproduct gold from domestic base metal ores is recovered as gold bullion at base metal refineries (*15*). Losses of gold in concentrating are about the same as those of the base metal but are negligible in smelting.

Gold is refined by chlorination in the molten state (Miller process) and by electrolysis (Wohlwill process). The latter process, used by the U.S. mints, gives a final bullion product 999.5 to 999.8 fine.

USES

Most of world gold production is absorbed by governments and central banks to provide stability for paper currencies and to settle international trade balances, but in recent years large quantities of gold have gone into private holdings. The chief nonmonetary uses of gold are in jewelry and the decorative arts, including watchcases, utensils, gold leaf, and decorative finishes on ceramics and other materials. Gold in various alloys with platinum-group metals is used in dentistry, for spinnerets in making synthetic fibers, thermocouples and electrical contacts, and in many types of scientific laboratory equipment. Gold also continues to find new applications in industry, particularly as protective and decorative coatings for other materials, and in recent years as coatings on ceramics and metals in architectural panels, as coatings on aircraft engine shrouds and earth satellites to provide protection against heat and corrosion, and for electrical components and circuitry where extreme reliability is required. Appreciable quantities of gold are consumed in established uses in the fields of optics, atomic energy, heat control and measurement, medical therapy, chemical manufacturing, and brazing.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Silver, always associated with gold to some degree in nature, is a coproduct of all gold mining; the average ratio by weight is about

1 part silver to 4 of gold. Crude platinum, sometimes present in gold placers, is recovered as a byproduct; in some areas in Colombia enough platinum is present that it becomes a coproduct. Platinum-group metals also occur in some lode gold ores. In the final refining of gold in the United States, a few thousand ounces of platinum-group metals are recovered annually.

The average recoveries of gold per ton from all base metal ores from which gold was recovered in 1963 were copper ore, $0.11; lead ore, $0.46; zinc ore, $0.07; and zinc-lead-copper ore, $0.56.

Uranium is recovered as a byproduct or coproduct of gold ores at several mines on the Rand in the Republic of South Africa and is a major source of revenue at some mines. From 5,000 to 7,000 ounces of osmiridium also are recovered annually as a byproduct of the Rand gold ores.

ALTERNATE MATERIALS

Alloys of the platinum-group metals such as platinum-iridium and palladium-ruthenium are substituted for gold in high-quality jewelry, watchcases, and other decorative articles, their use being determined largely by popular demand and vogue. The various metals and their use in place of gold include platinum and palladium separately or alloyed with gold for various appliances in dentistry; platinum leaf (for gold leaf) for signs and decorative designs; and stainless steel, chromium, and nickel alloys, in corrosion-resistant equipment. The quantity of gold displaced by substitution of other materials is small, however, compared with the consumption of gold in the arts and industry.

SECONDARY SOURCES

Because of the indestructibility and high value of gold, there is a high return from old jewelry, watchcases, optical frames, dental crowns, and laboratory ware. The secondary metal recovered by refiners can be of the same high quality as primary metal. According to the Bureau of the Mint, scrap gold returned from industry annually averaged about 950,000 ounces during 1959–63.

RESERVES

A preliminary estimate of domestic gold reserves, based on data compiled in a current study of the Nation's gold potential, shows a total of 20 million ounces of gold, virtually all of which is recoverable under current economic and technologic conditions. This reserve comprises 1 million ounces in placers, 5 million ounces in lode gold ores, and 14 million ounces in base-metal ores, mostly in large low-grade copper ores.

The current estimate of domestic gold reserves is based on a reserve study made in 1944 (*3*) with allowance made for subsequent production, new discoveries, and losses due to increased production costs.

One substantial new discovery in Nevada is expected to produce about 1 million ounces. New discoveries and favorable economic conditions have resulted in an increase of 15 million ounces in the estimated recoverable byproduct gold from base-metal ores. It is estimated that byproduct gold production will continue at the present rate for 30 years. The unfavorable economics of placer and lode gold mines is significant—dredges in California will exhaust economically minable gravel in less than 5 years. The profit margin at the Nation's major lode producer has declined to a low level, and unless the decline is arrested operations might be terminated in 5 years.

Reliable data on gold reserves in many countries are nonexistent or unavailable. Gold reserves in the Republic of South Africa are estimated to total more than 500 million ounces of which about 90 million ounces is in fully developed ore blocked out at the end of 1963. An additional 4 million ounces is contained in pillars and dumps, most of which may ultimately be recovered. Reserves of gold in ore and placer deposits in the U.S.S.R. are believed to be large; some significant new discoveries have been reported but detailed data are not available. In recent years increases in gold reserves resulting from new ore discoveries and extensions of known ore deposits, particularly in South Africa, have helped to offset declines in other principal gold-producing countries. The world reserve of recoverable gold may approximate 1 billion ounces, with about 75 percent in gold ores and placers and 25 percent in base metal ores.

Although gold is present in only minute unit quantity in sea water and the problem of extraction is unsolved, analytical experiments indicate that a cubic mile of sea water contains 130 to 260 tons of gold, equivalent to 3.8 to 7.6 million ounces.

Monetary gold reserves of the principal free world central banks and governments and international banking institutions at the end of 1963 aggregated $42.3 billion (*6*). It is estimated that an additional $15 billion in gold is held in private stocks. Estimates of the gold reserve of the U.S.S.R. range from about $1.8 billion to $10 billion.

The U.S. gold reserve of about $15.6 billion at the end of 1963 constituted about 37 percent of the total official reserves of the free world.

Gold reserves of other principal free world countries, in billions of dollars, at the end of 1963 were West Germany, 3.8; France, 3.2; Switzerland, 2.8; United Kingdom, 2.5; Italy, 2.3; Netherlands, 1.6; Belgium, 1.4; and Canada, 0.8. The International Monetary Fund reported gold reserves of $2.3 billion.

SOURCES OF STATISTICAL INFORMATION

In the United States, statistics on the domestic mine production of gold are gathered, analyzed, and compiled by the Bureau of Mines in cooperation with the geological surveys of some States. Monthly and annual reports are published. Data on refinery production and on domestic and foreign consumption in the arts and industries and coinage are compiled and published by the Bureau of the Mint, U.S. Treasury Department. Data on consumption of gold by principal industrial uses are compiled semiannually by the Office of Gold and Silver Operations, U.S. Treasury Department. Foreign trade data on gold ore and bullion are published by the U.S. Department of Commerce. Comprehensive data on gold transactions of the free world countries and international institutions, including net gold purchases and estimated gold reserves of central banks and governments, are compiled and published monthly by the Board of Governors of the Federal Reserve System. Monthly bulletins of the U.S. Treasury Department publish detailed data on U.S. monetary gold stocks and banking transactions related to gold.

The Bureau of Mines also compiles data on gold production in foreign countries. Detailed data on gold production are published by some foreign countries, especially those of the British Commonwealth, but corresponding data for other countries are not complete. No data on gold production or reserves are published by the U.S.S.R. or the other Communist nations.

PRODUCTION, CONSUMPTION, AND TRADE

The total world gold production from 1493 to 1963 is estimated at 2,118 million troy ounces. Peak annual production prior to World War II was 42.2 million ounces in 1940. Since World War II, world gold production has steadily increased, reaching a total of 44.3 million ounces valued at $1.55 billion in 1963 (fig. 1). The gain in world output was due principally to the remarkable growth in gold mining in the Republic of South Africa. In recent years the United States has ranked fourth in gold production, exceeded by the Republic of South Africa, Canada, and the U.S.S.R. In 1963 U.S. production (fig. 2) was 1.45 million ounces; total output to the end of 1963 was 304.02 million ounces, or 14 percent of the world total since 1493.

Of the cumulative quantity of gold produced from the earth, it is estimated that 55 percent is held by governments and central banks, 30 percent is held by corporations and individuals, and 15 percent has been dissipated or lost.

During 1959–63 net consumption of gold by industry and the arts in the United States was nearly double domestic production. Estimated consumption of gold in the industries and arts of the principal free world countries in 1963 was about 9.3 million ounces; that used in coinage totaled 0.45 million ounces (*2*).

During 1963, the United States imported gold ore, base bullion, refined bullion, and gold coins from 23 countries and exported these items to 7 other countries. Refined bullion comprised the bulk of the imports and exports. In 1963 Canada supplied nearly one-half of the gold imports; Colombia and the Philippines supplied most of the remainder. Of the total gold exported in 1963, about 70 percent went to France and 28 percent to the United Kingdom. Prior to 1961 imports of gold greatly exceeded exports, but 1961–63 exports increased sharply, exceeding imports by a wide margin. The United States imposes no duties on gold imported in ores or bullion but does levy duties ranging from 30 to 65 percent ad valorem on manufactured goods. The volume of imports of such gold merchandise is relatively small, however.

STRATEGIC CONSIDERATIONS

Although there are not many industrial uses of gold that are indispensable to the military services, the U.S. gold reserve is strategic and important in maintaining fiscal solvency, since gold is the monetary base for currency and the standard for settlement of international trade balances.

The reserve of gold-bearing ores in the United States is enough to maintain production near the current rate for several years under a cost-price relationship near the present level. Moreover, domestic gold consumption in the arts and industry will probably continue to exceed production in the near future (table 1). The deficit in domestic supply will be balanced by sales from the Treasury stock; how-

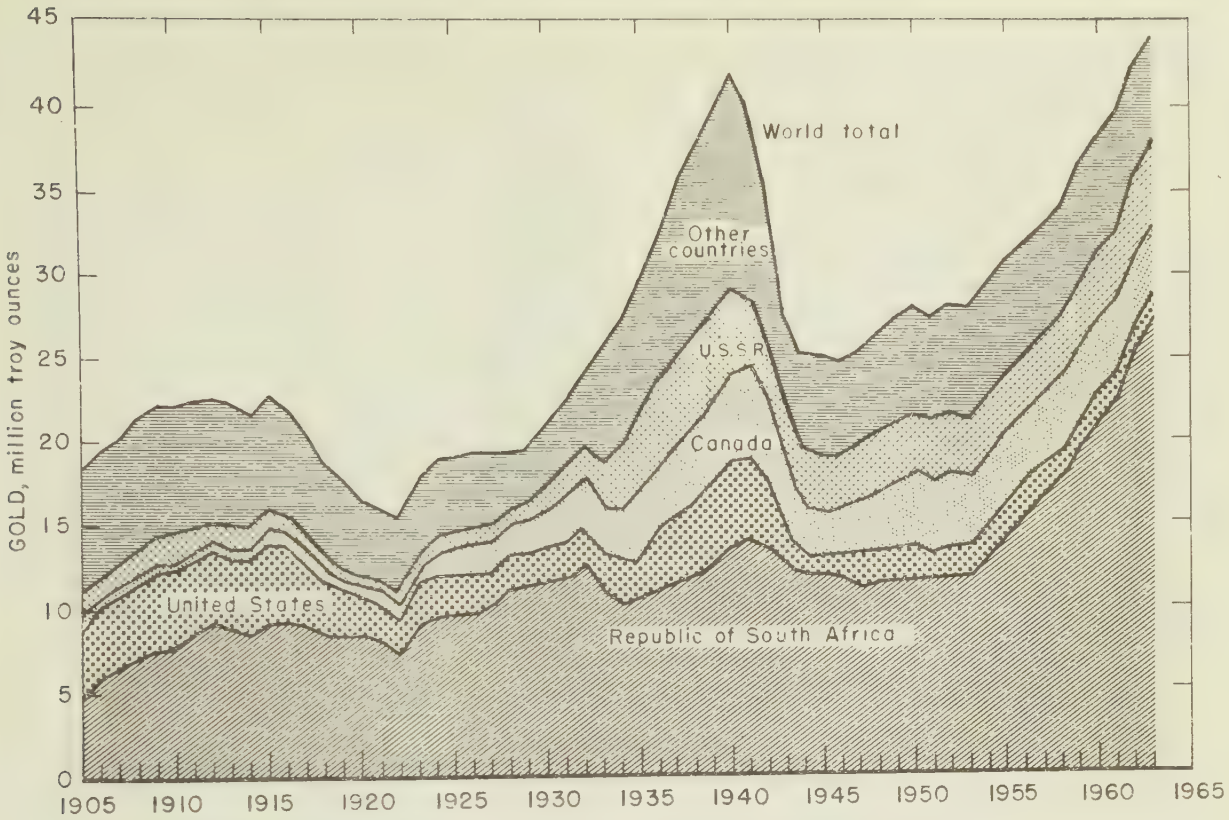

FIGURE 1.—World Gold Production.

ever, this stock is declining steadily as withdrawals are made in connection with settlement of adverse trade balances. Imports of gold into the United States are shown in table 2.

TABLE 1.—*Net industrial consumption of gold in the United States* [1]

[Thousand troy ounces]

Year	Issued for industrial use	Returned from industrial use	Net industrial consumption
1954–58 (average)	2,247	796	1,451
1959	3,176	654	2,522
1960	3,700	700	3,000
1961	3,913	1,138	2,775
1962	4,486	910	3,576
1963	4,252	1,332	2,920

[1] Including consumption in the arts.

Source: Bureau of the Mint, U.S. Department of the Treasury.

TABLE 2.—*Value of gold imported into and exported from the United States*

[Thousands]

Year	Imports	Exports
1954–58 (average)	$167,667	$50,981
1959	304,378	1,933
1960	335,032	1,647
1961	56,211	775,001
1962	150,932	380,962
1963	44,414	203,784

Source: Bureau of the Census.

GOVERNMENT PROGRAMS

The most far-reaching U.S. Government policy affecting gold is the establishment of the gold parity of the dollar. A firm policy of maintaining the $35 rate has been expressed

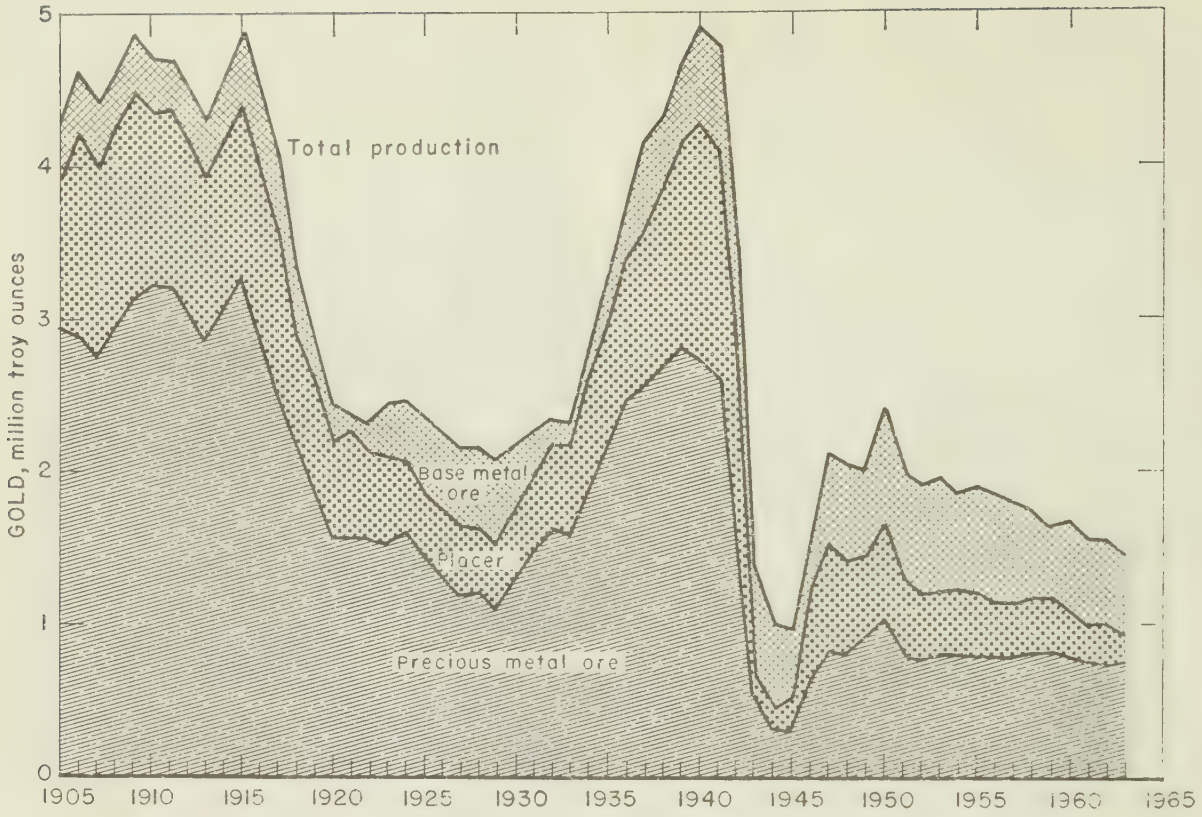

FIGURE 2.—U.S. Gold Production.

repeatedly since World War II. This price forms the basis for the official world price because the United States stands ready to purchase all gold offered at $35 per ounce.

The most recent statement of policy concerning the price of gold was made by President Johnson in his Economic Report to the Congress in January 1965.

> There can be no question of our capacity and determination to maintain the gold value of the dollar at $35 an ounce. The full resources of the Nation are pledged to that end.
>
> Clearly, we should place beyond any doubt our ability to use our gold to make good our pledge to maintain the gold value of the dollar at $35 an ounce with every resource at our command.

Transactions in gold are subject to government regulations that require gold bullion and gold coins to be delivered to U.S. Treasury institutions. Licenses are issued by the Treasury Department permitting purchases, sales, imports, and exports of gold for use in the arts and industries.

The government program of financial aid administered by the Office of Minerals Exploration provides for loans to explore gold deposits up to 50 percent of the total cost of such exploration. The loan is repaid by a 5-percent royalty on any production from the property.

Since 1948 the Canadian Government has granted financial assistance to marginal or high-cost gold mines under terms of the Emergency Gold Mining Assistance Act (EGMAA) to help them meet the greatly increased cost of production after World War II. The subsidy program under EGMAA was extended with certain amendments through 1967. Similar cost-aid subsidies in Australia and tax concessions in Australia and the Republic of South Africa have aided some marginal gold mines. Most foreign governments have permitted gold producers to benefit by selling part of their output at premium prices in the free market.

PRICES

After being $20.67+ per fine troy ounce for nearly a century, the price of gold was raised to $35 per ounce by Presidential proclamation in January 1934 and has remained unchanged since then. Presidential power to revalue gold lapsed in 1943; only an act of Congress can change the gold parity of the dollar. During and after World War II, hoarding in various parts of the world increased demand, and some gold was sold in free markets developed outside the United States; prices were substan-

tially higher than the official $35 per ounce. When restrictions on the sale of gold were relaxed by some foreign countries and by the International Monetary Fund (1951), part of the world production was sold at free market prices. The not always realistic higher prices in some of these markets reflect the difference between official and free market foreign exchange rates.

In 1963 the price of gold on the London exchange (where most of the gold trading is done) fluctuated in a narrow range close to the official U.S. price of $35 per ounce, owing principally to the stabilizing operations of the Bank of England on behalf of the international gold pool and the bank's handling of the sale of South African gold. In 1963 the price of bar gold in most world markets was only slightly higher than the London price, except in markets that reflected local trading and monetary habits and that used inconvertible currency.

Before gold was revaluated in 1934, world production at the former price, $20.67+ per ounce, had been declining for many years because of rising costs and depletion of ore reserves. Stimulated by the $35 price, gold mining again flourished and many countries set new production records in the late 1930's and early 1940's. During World War II gold mining declined in most countries because of restrictions, shortage of labor and supplies, and higher costs. In the postwar years steadily rising costs in relation to the fixed price of gold made several gold mines in the United States unprofitable. Most large lode gold mining companies of the world continued to mine their higher grade reserves profitably, but many small mines closed. Base-metal mines that yield byproduct gold were not greatly affected by the fixed price of gold because the increased price of base metals tended to offset the increased cost of mining.

TAXES

The gold mining industry in the United States generally is taxed the same as other industries. The depletion allowance for gold is 15 percent. Some countries impose a production or export tax on gold that may add to the mining cost; others promote gold mining by tax concessions.

RESEARCH

The processes of recovering gold from ores, particularly amalgamation and cyanidation, have attained high metallurgical efficiency owing to extended operating experience and research by commercial laboratories, manufacturers, and mining companies on chemical reagents, design of machinery, and procedures. Research is necessary to adapt the basic processes to the peculiarities of some ores and to meet special conditions, and such research is done by mining companies and ore-testing laboratories.

Recent investigations by the Canadian Mines Branch in cooperation with the gold mining industry have yielded useful results and have shown how metallurgical efficiency in treating some ores can be improved by the adoption of modern scientific techniques.

Fundamental studies of gold milling processes and possible automation of operations to increase productivity and to lower costs are constantly being studied by gold mining companies in many parts of the world.

Bureau of Mines basic research yields information that contributes to greater efficiency and safety in mining, better evaluation of mineral resources, and increased recovery of ores and metals from mineral deposits. These fundamental studies aid gold mining as well as other types of mining.

Research on the cyanidation and chloride volatilization of refractory gold ores was conducted by the Bureau during 1918–28; the carbon-cyanidation treatment of gold ores proved commercially feasible in more recent investigations (*19*). Recent metallurgical research by the Bureau included applying ultrasonic principles to amalgamation and cyanidation to improve efficiency and recovery of gold.

OUTLOOK

U.S. production of gold should hold fairly steady near the 1963 output in the next few years and then decline slowly as production costs continue to rise and economically minable reserves at gold mines gradually become depleted. New production in Nevada will probably offset decreased production in other areas in the near future. Byproduct gold production from base-metal mines probably will continue at about the current level.

The rising trend in world gold production should continue in the next few years as output from South Africa, which constitutes more than one-half of world production, continues to grow. Continued expansion of output at new mines in the Orange Free State and in the Far East and Far West Rand areas in the Transvaal will be offset to some extent by a falloff in production in the Central Rand owing to depletion of economically minable reserves at some of the older

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mines. Although South African gold production has been rising for the past 12 years and establishing record highs, it is believed that output is approaching a maximum level and will probably begin to decline within the next decade. The gold mining industry in South Africa accounts for about 45 percent of the country's exports and receives substantial financial assistance from the Government, principally in the form of loans, tax concessions, and amortization allowances. Gold production in Ghana has been rising in the last few years reaching an alltime record in 1963, but output in Canada and Australia has been slowly declining, in spite of subsidies and other forms of Government aid to the gold mining industry.

Although gold is used primarily as a monetary reserve of government central banks to stabilize currency and to settle international trade balances, world authorities disagree on requirements for monetary gold. Anticipated additions to the gold reserves of free world countries will depend chiefly on such factors as new production, gold sales by the U.S.S.R., demand for gold in the arts and industries, demand for private investment, and hoarding. In recent years more than half of the new gold production was absorbed by private interests. Official gold stocks have increased by only 1.3 percent annually over the past 15 years owing to sustained private demand. Operations of the gold pool supplemented by sales from the U.S.S.R. will continue to be principal factors in providing sufficient gold to meet all demands and in maintaining a stable price in world markets.

Consumption in domestic industries and the arts has been increasing, largely owing to increased use of gold in modern science and technology. New applications in industry and in defense-oriented equipment will continue to be developed, based essentially on gold's superior malleability, ductility, resistance to tarnish, and high reflectivity. The growing use of gold as a protective coating on other, less-resistant materials is significant. These coatings, which are sprayed or electrodeposited, provide oxidation resistance on space vehicles and in electrical components as well as providing decorative and corrosion-resistant finishes on a wide variety of commercial products.

Investigations being conducted by the Committee for Research on the Properties and Uses of Gold, Inc., may lead to increased industrial use of gold as new applications are developed. Growth of established, traditional uses of gold in jewelry and the decorative arts will probably parallel the growth in gross national product and population.

Although advances in science and technology may lead to new and improved prospecting techniques, new sources of gold will be discovered less frequently, as economic conditions in the industry become progressively less favorable and incentive for prospecting and exploration for gold continues to decline. Some new sources probably will be discovered in South Africa, the U.S.S.R., and Canada, but no significant new discoveries can be expected in the United States under present economic conditions.

It is difficult to forecast the quantity of gold required annually to meet monetary requirements and to provide reserves adequate for international liquidity. Some authorities believe that the monetary reserves of the free world are too low in purchasing power to provide full mobility for trade and capital. The U.S. gold reserve has been declining in recent years and those of Western Europe have been increasing as a result of balance-of-payments transactions. However, the high rate of outflow of gold from the U.S. reserve may have been arrested in the past 2 years as the U.S. balance-of-payments position shows signs of improving and stabilizing operations of the International Monetary Fund and the International Gold Pool become more effective.

PROBLEMS

The paramount problem facing the domestic gold mining industry is one of survival in the face of rising costs and a fixed price of its product. This pattern has resulted in closing most of the gold mines in the United States, and has been repeated throughout the world. In all places except South Africa and possibly Ghana, it has resulted in reduced profits, loss of ore reserves, and depression in the gold mining industry. Revaluation of gold in terms of dollars, or a substantial reduction in the cost of production, could revive the industry. However, fixing the price of gold in the Nation is mainly a monetary rather than a commodity problem.

The problem of rising costs due principally to the effect of inflationary factors has been partly offset at some mines by technological improvements and operating economics; however, further savings in the foreseeable future appear unlikely and reserves of minable ore at the relatively few operating mines remaining will probably diminish unless there is some unforeseen change in production cost or the price of gold.

The resource base of the domestic gold mining industry has been depleted by more than 100

years of intensive exploitation, when most of the high-grade, easily accessible ore was mined. The industry's problems were intensified by the closing of mines in World War II and subsequent high cost of rehabilitation. Many mines that were operating prior to the closing order were unable to restore production when the order was rescinded.

Other basic problems are related to the small size and wide distribution of many deposits. The vein-type source and ground conditions of most gold mines preclude the use of large-scale equipment successful in reducing costs in base metal mines.

Consumption of gold in the domestic arts and industries has exceeded mine production since 1957, and the deficit in new supply is increasing as production continues to decline. Hence, a long-term domestic gold problem is to find and develop new supply sources to balance the growing industrial demand.

Many technologic problems of gold mining are common to other underground mining operations—basically they are cost problems inherent in breaking hard siliceous rock sometimes deep within the earth's crust, transporting it to milling and processing plants, and extracting minute quantities of contained gold.

Deficiencies exist in statistics on industrial consumption of gold, which are needed by producing and consuming industries and by government in formulating policy, assessing trends, and estimating future demand. Data on end use and quantities used in various industries are incomplete or totally lacking, and this deficiency is a serious handicap in developing a comprehensive program for gold.

Problems of monetary reserves and liquidity are concerned chiefly with supplying the gold required for expanding world trade and involve international political and financial policies.

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GRAPHITE

By John W. Cole [1]

GRAPHITE mining in the United States always has been a small scale industry, and significant expansion in production has occurred only in wartime under government subsidy. In 1963, domestic graphite was produced only in Texas. Foreign deposits occur over a wide area; those in the Malagasy Republic, Ceylon, and Mexico provide most of the graphite consumed in the United States.

The three major types of natural graphite are lump, amorphous, and flake. All three types are mined underground by conventional mining methods, although most flake graphite is mined by open pit methods. Hand cobbing and sorting are the major steps in preparing Ceylon lump graphite for market. Amorphous graphite requires only crushing or grinding to the desired particle size. Flake graphite must be concentrated and refined before marketing. Special grades of high-purity graphite are produced by chemical treatment.

Manufactured graphite is produced from petroleum coke by baking at about 950° C and subsequently graphitizing at about 2,800° C. Graphites with special properties, such as oriented and recrystallized types, are being developed for use in space-age applications and as more knowledge of them is obtained, their use is expected to grow.

Although some interchangeability is possible among all types of natural graphite and between natural and manufactured graphite, there is no satisfactory substitute for graphite in most applications. Silicon carbide-graphite crucibles have reduced the need for coarse-flake graphite, and some high-temperature refractory materials such as nitrides, borides, and silicides may be suitable replacements for clay-graphite crucibles requiring coarse-flake graphite.

Potential domestic resources of flake graphite are large but low in tenor. Amorphous graphite, although abundant in the United States, is of poor quality. World graphite resources of all types are enoromous.

The principal uses for natural graphite in 1963 were foundry facings (36 percent), steelmaking (16 percent), lubricants (14 percent), and refractories (11 percent). The use pattern varies widely for the major types of graphite.

Although the United States could achieve self-sufficiency in crystalline flake graphite, the cost would be two to three times the normal market price of Malagasy flake. Moreover, about 1,000 short tons a year of Ceylon 97 to 98-percent carbon amorphous lump would still be required for strategic uses. Stockpile objectives have been achieved for strategic and critical grades of natural graphite.

The short- and long-term supply outlook for all types of imported graphite required for the U.S. economy is favorable, and domestic production could be expanded if necessary. There is no indication of a major increase in requirements for natural graphite. Manufactured-graphite production facilities are adequate for present needs.

Problems of the natural graphite industry include the limited market for graphite of each type and the reluctance of consumers to use graphite from untried sources. Major technologic problems include determining the interchangeability possible among various types of graphite and increasing U.S. self-sufficiency. A major problem of the manufactured-graphite industry has been the inability to produce graphite to stringent specifications.

[1] Commodity specialist.

BACKGROUND

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

From 1910 through 1963 the number of domestic graphite producing mines ranged from 42 (in 1918) to 1 (in 1932, 1940, 1962, and 1963), and annual production ranged from less than 500 to 13,600 short tons. Some domestic production has been reported every year since 1884, but apparent consumption has ranged from 5 to more than 15 times domestic production. The history of the domestic graphite-mining industry is thus reflected to have been one of short periods of production, under the stimulus of Government subsidy during wartime, to long periods of inactivity for most individual deposits.

Only one domestic producer continued to operate in 1963. Southwestern Graphite Co., Burnet, Tex., produced small-flake crystalline graphite from weathered graphite schist containing about 5 percent graphite, from an open pit mine.

Graphite recovered from milling the ore is sized and graded by carbon content into more than 20 different grades. Final products are shipped directly to consumers throughout the United States.

Graphite has been reported in 25 states in the United States, and 17 have produced it in commercial quantities (*1*).[2] Flake graphite has been mined in Alabama, California, Massachusetts, New Jersey, New York, Pennsylvania, and Texas. Amorphous graphite has been mined in Colorado, Georgia, Michigan, Nevada, New Mexico, North Carolina, Rhode Island, Utah, and Wisconsin. A small quantity of lump graphite has been mined near Dillon, Montana.

Graphite deposits occur in virtually all countries; the foreign deposits of most importance to the United States economy are the lump deposits of Ceylon, the amorphous deposits of Sonora, Mexico, and the crystalline flake deposits of the Malagasy Republic.

Mexican companies, some of them affiliated with U.S. firms, mine 80- to 93-percent carbon amorphous graphite from underground mines in Sonora, Mexico. Most of the output is exported to the United States. Ore is sorted into grades, crushed, and shipped in carlots to end-use customers or to U.S. plants for additional treatment.

Graphite is imported from the Malagasy Republic, Ceylon, Norway, West Germany and other foreign sources. Importers grind and blend graphite to consumer specifications. Manufactured graphite powder and shapes are produced by 5 firms in 10 plants: 3 are situated in New York, 2 in Pennsylvania, and 1 each in California, Michigan, North Carolina, Tennessee, and West Virginia.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Graphite, a form of carbon that crystallizes in the hexagonal system, also has been referred to by industry and in publications as plumbago and black lead.

The three major types of natural graphite, based on geological occurrence, are lump (from vein deposits), amorphous (from metamorphosed coalbeds), and crystalline flake (from layered metamorphosed rocks).

The terms "amorphous" when applied to graphite is a misnomer; all graphite is crystalline, but the type designated as amorphous is so fine grained that individual crystals cannot be distinguished by the unaided eye. The definition of amorphous, as applied to graphite, has been further complicated by longstanding industrial application of the term to very fine particles of crystalline flake graphite that can be sold only for low-value uses, such as foundry facings, and its application to the fine-grained varieties of Ceylon lump graphite. These fine-grained varieties of lump can be reduced easily to fine particle size by grinding. They are called amorphous lump to distinguish them from tough, platy, and acicular varieties, known as crystalline lump, that can be reduced in particle size only with extreme difficulty.

Paragraph 213 of the Tariff Act of 1930 defines crystalline flake graphite as follows:

> As used in this paragraph, the term "crystalline flake" means graphite or plumbago, which occurs disseminated as a relatively thin flake throughout its containing rock, decomposed or not, and which may be or has been separated therefrom by ordinary crushing, pulverizing, screening, or mechanical concentration process, such flake being made up of a number of parallel laminae, which may be separated by mechanical means.

Under the foregoing definition finely divided particles of crystalline flake graphite would be classified as crystalline graphite. However, the

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

Court of Customs Appeals has repeatedly held that commercial designations and not scientific terms must govern classification and that when a commercial meaning differs from the common meaning the commercial designation must govern. Thus, large quantities of fine crystalline flake graphite are imported under the amorphous classification.

Ceylon lump graphite, as previously stated, is classified as amorphous or crystalline. Each type is divided into a number of grades, depending upon the particle size (lump, ranging from the size of walnuts to that of peas; chip, from the size of peas to about that of wheat grains; dust, from 40- to 60-mesh; and flying dust, finer than 60-mesh), graphitic carbon content, and degree of consolidation (*7*).

Amorphous graphite is graded primarily on graphitic carbon content. Commercial ores contain about 50 to 93 percent carbon, depending on their source.

Crystalline flake graphite from the Malagasy Republic is divided into two main grades, "flake" (coarse flake) and "fines" (fine flake). Malagasy crucible flake must have a minimum of 85 percent graphitic carbon and be essentially all minus 8- plus 60-mesh. Other crystalline flake graphites are graded according to graphitic carbon content and particle size.

The terms "manufactured," "artificial," "electric-furnace," and "synthetic" are used to describe graphite produced from coke.

TECHNOLOGY

Geology (*1*)

The classification of natural graphite into three principal types is based on physical characteristics that are due to major differences in geologic origin and occurrence.

Lump graphite occurs as fissure-filled veins. It is typically massive, ranging in particle size from extremely fine grains (amorphous) to coarse, platy intergrowths or fibrous to acicular aggregates (crystalline). The origin of vein-type graphite deposits is believed to be either hydrothermal or pneumatolytic. The veins cut different types of igneous and metamorphic rocks; apparently the nature of the host rock bears no genetic relationship to the veins. Minerals occurring as impurities with the graphite include feldspar, quartz, mica, pyroxene, zircon, rutile, apatite, and iron sulfides. These impurities usually form isolated pockets or grains in the veins.

Amorphous graphite is formed by metamorphism of coalbeds by nearby intrusives. The graphite from these altered coals is extremely fine grained, soft, dull, black, earthy-looking, and usually somewhat porous. Its purity depends on the purity of the original coalbeds. Amorphous graphite usually is associated with sandstones, shales, slates, and limestones. Accessory minerals include quartz, clay, and iron sulfides.

Flake graphite commonly occurs disseminated in regionally metamorphosed sedimentary rocks, such as gneisses, schists, and marbles. It is believed that the graphite was formed under the same conditions that caused the metamorphism of the rocks—from carbon deposited with the sediments.

Although the flake graphite deposits of the Malagasy Republic conform to this description, the commercial deposits that are exploited are alluvial, lateritic cover that has accumulated at the surface (*13*). The graphite, quartz, and other resistant minerals have been freed by kaolinization of the feldspars. Laterization extends to a depth of several meters. The grade of ore usually is 5 or 6 percent graphite.

Mining

In Ceylon, lump graphite is mined underground from narrow, steeply dipping veins. The ore is mined principally by overhand stoping and filling, using temporary stulls when necessary to support the walls. Hand drilling is used in most stoping to achieve selective mining and to avoid unwanted fines and product contamination. Air drills are used in development headings. Minor sorting is done at the mine on the surface. The ore is hauled by truck to the sorting and classification yard.

Amorphous graphite beds usually also are mined underground, but the beds are much thicker than those of amorphous and crystalline lump. The ore is drilled, blasted, hand-loaded in cars, and brought to the surface by conventional methods.

Flake graphite deposits have been mined by underground and surface methods. Usually underground deposits are in unweathered ore and require drilling and blasting. Most surface mining is confined to the weathered part of the deposit, and normal excavating equipment, such as power shovels, bulldozers, and scarifiers, is used with a minimum of drilling and blasting.

Mining at the property of the Southwestern Graphite Co. near Burnet, Tex., is conducted by open pit methods. Sixteen foot benches are drilled for blasting by use of wagondrills. The rock is hard and tough; much secondary blasting is required. The ore is hauled to the mill by use of motortrucks.

In the Malagasy Republic the graphite ore is transported by hydraulic methods. Water is

brought many miles by ditches and flumes to the top of the deposit selected for mining. The soft, weathered ore is fed by hand or bulldozers into the flowing water and carried by a flume or canal to a mill less than a mile away in the valley below. Overburden is removed in the same manner but bypassed around the mill. The swiftly flowing water not only transports the ore, but the resulting slaking and tumbling action breaks the clay-like material and serves as the first step in separating the graphite from the gangue.

Milling

Ceylon amorphous and crystalline lump graphites are refined by hand cobbing and sorting, and wiping lumps on wet burlap to remove fines. The chip and dust grades are machine-sorted in revolving trommels. Light hand sorting and cleaning operations are done by women while the heavier duties are performed by men.

Most amorphous graphite that requires concentrating is not worth mining. Preparation for most uses requires grinding only, and coarse impurities are removed by screening or air separation methods. Recently a new flotation plant was installed in Austria to upgrade microcrystalline graphite to a grade ranging from 80 to 92 percent carbon with a particle size range of 0.005 to 0.008 inch. This plant is reported to be the first flotation plant in the world to be successful in enriching microcrystalline (amorphous) graphite (*3*).

Flake graphite from disseminated deposits must be concentrated to meet market requirements. Virtually every known concentrating device and combination of separating principles have been tried. Probably in no other industry has such a large proportion of the mills failed to make commercial recoveries. Many so-called secret processes have been used to concentrate graphite, and the mineral has gained a reputation of being difficult to concentrate. Actually, it is one of the easiest minerals to segregate into a rough concentrate but one of the most difficult to refine.

As a premium is placed upon the grain size of flake graphite, the problem in milling is one of grinding to free the graphite without reducing the flake size excessively. This is difficult because graphite flake during grinding is cut by quartz and other sharp minerals in the gangue, thus reducing flake size rapidly. However, if the flake can be removed from most of the quartz and other sharp minerals soon enough, subsequent grinding will usually reduce the size of the remaining gangue, with little further reduction in the size of the flake. Impact grinding of essentially pure flake in a ball mill reduces flake size rather slowly. The grinding characteristics of flake graphite under these conditions are similar to those of mica.

Graphite is a natural floater and does not require a collector; hence flotation has become the accepted method for beneficiating disseminated ores. High recoveries are common, but acceptable graphitic carbon contents are difficult to attain. The main problem in separation is to depress the gangue. Fine graphite smeared on the surfaces of relatively pure particles of quartz, mica, and other gangue minerals makes them floatable, necessitating repeated cleaning to permit recovery of high-grade products.

Regrinding a rougher concentrate reduces the number of cleanings needed. The difficulty in obtaining high-purity products from natural flake stems from the fact that much of the flake either has a siliceous skeleton (which can be seen when the carbon is burned) or is composed of a layer of mica between outer layers of graphite. Sometimes it is impossible to obtain high-grade material.

In the Malagasy Republic (*13*) graphite ore from the flume or canal flows over a screen or grizzly with 5 to 10 mm spacing. Oversize is discarded. Undersize passes through a decantation tank. The mud overflows while graphite and sand settle to the bottom. Graphite in the mud is recovered by washing on 60 to 80 mesh screens. Mud is washed through the screen and the graphite and sand is discharged from the top. Graphite is recovered from the sand by flotation. A crude graphite product containing 65 to 80 percent carbon is recovered from the washing plant at the mine. This product is shipped to a central refining plant where it is ground in ball or rod mills, refloated, screened, and blended into specification grades. The final products are plus-60 mesh flake containing 85.0 to 87.5 percent graphitic carbon, and minus-60 mesh material that contains 90.0 to 92.5 percent. A generalized flowsheet of washing and refining is shown in figure 1. General operating data are summarized as follows:

Water used in mining and treatment: 8 to 12 cubic meters per cubic meter of ore.

Installed power: 1 to 2 horsepower per ton of graphite produced monthly.

Labor performance: 20 to 50 kilograms graphite per man-day.

Some flotation concentrate for high-purity products is refined by further comminution in rolls or burrstones followed by screening, but this method is said to be inferior to controlled regrinding in ball mills followed by reflotation. Graphite with a purity exceeding 99 percent may be produced by chemical treatment of lower grade material with hydrofluoric acid or sodium hydroxide to remove silica. How-

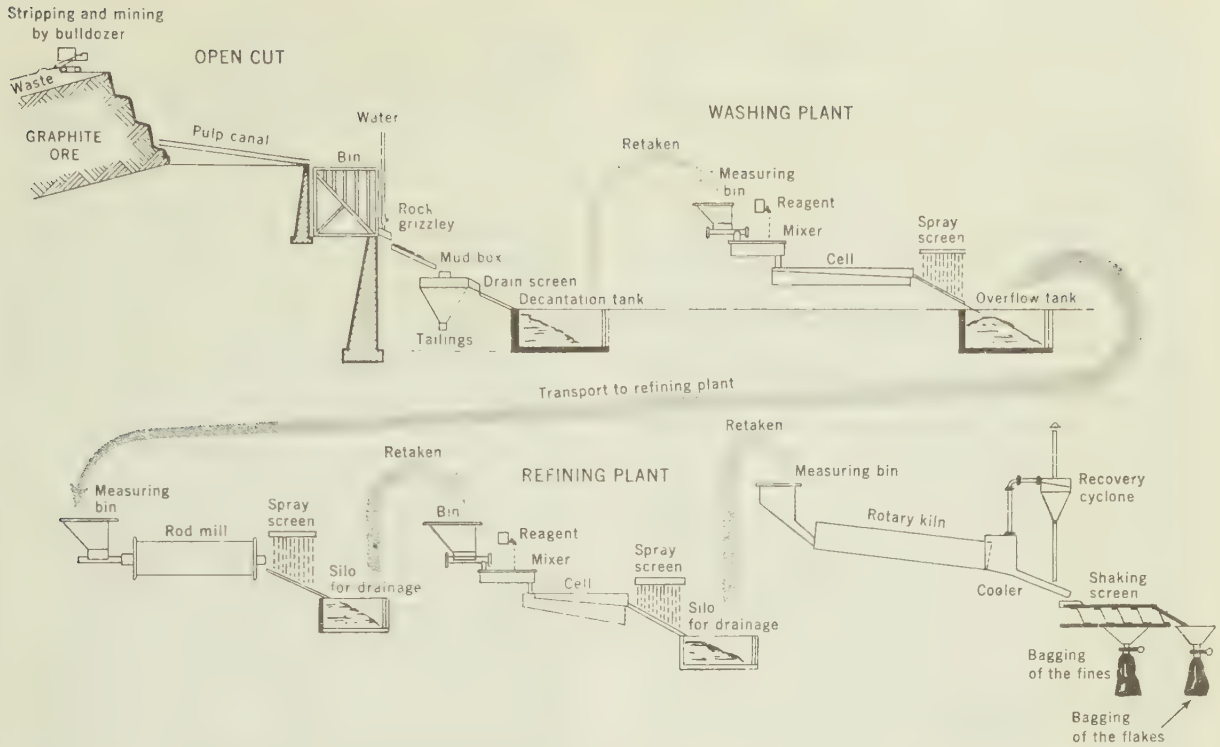

FIGURE 1.—Generalized flowsheet of Malagasy graphite mining and beneficiation.

ever, this treatment is expensive and is practiced commerically only in West Germany and France, and on an extremely small scale.

Manufactured Graphite (*6*)

The principal raw materials for manufacturing carbon and graphite products are petroleum coke, coal tar pitch binder, and a small quantity of petroleum-base oil to facilitate extrusion. The raw materials are simultaneously heated to about 150° C and thoroughly mixed, cooled to 100° C, extruded or molded to form the desired shapes, and baked at 950° C. The length of time the material is in the baking furnace varies with the quantity and size of the shapes, but usually is 11 to 13 weeks. After cooling, the carbon shapes are completed. Shapes to be converted to graphite are then transferred to graphitizing furnaces and heated to about 2,800° C to form soft, unctuous graphite. This operation, including heating, soaking, and cooling, requires 4 to 5 more weeks. The graphitizing takes place largely because of the temperature, but virtually all of the metal oxides (except part of the vanadium) in the raw carbon are reduced to metal and vaporized. Consequently, the graphitizing process is also a refining step.

During graphitizing, the electrodes and other shapes are packed in granulated or powdered metallurgical coke or graphitized material that has already gone through one or more furnace cycles. Part of this granular and powdered manufactured graphite is then sized and marketed.

Manufactured graphite varies considerably in physical and chemical properties, depending on the quality of the petroleum coke, grade and quantity of pitch, degree of preferred orientation imparted to the coke particles during extrusion, and maximum temperature and period of heating. The variables are too numerous and their interrelationship is not well enough understood to enable the routine manufacture of a product to close specifications.

Pyrolytic graphite is produced by thermal decomposition of a hydrocarbon gas in an evacuated chamber of absolute pressure of 4 to 6 mm of mercury by contact with a base (substrate) material of graphite that is maintained at an elevated temperature (plus 3,000° F). The carbon is deposited on the substrate as graphite crystals with the *a b* axial directions parallel to the surface of the substrate. Because of this crystal orientation, pyrolytic graphite is highly anisotropic. The mechanical strength, and electrical and thermal con-

ductivities parallel to the surface of the substrate is many times the value of these properties normal to the surface.

Graphite whiskers (single crystals) have been grown that have a tensile strength of 3 million pounds per square inch. This compares with a strength of 2 million pounds per square inch for iron whiskers.

Various grades of manufactured graphite are produced. Each manufacturer has a series of number and letter designations for his product. Special grades for nuclear applications are processed in the same manner as commercial grades, except that raw materials are more carefully selected and petroleum coke is used as a packing material during graphitizing instead of metallurgical coke (*10*).

Pyrolytic graphite is becoming available in limited quantities for experimental purposes. It is being used as structural and coating material where its relative hardness and anisotrophy are valuable. It is finding uses in the missile industry as rocket-motor nozzle liners and nose cones. It also may be used in the high-temperature reactor field as a low permeability coating for fuel elements.

Recrystallized bulk graphite also is in production. It has high strength at high temperatures and it has less creep at 3,000° C than conventional graphites have at 2,500° C. Recrystallized graphite shows superior performance in rocket-motor nozzles. It has good dimensional stability under neutron-radiation.

Fibrous forms of graphite—thread, yarn, felt, and cloth—now are available. They are finding application as thermal insulation, electric heaters, and as reinforcement for structural elements made of plastics or resins. Wooly and foam types of graphite also are available for use as high-temperature heat insulators.

USES

The major strategic use for Ceylon amorphous lump is for carbon brushes, for fractional horsepower motors and other electrical equipment, for high-altitude military aircraft and submarines, and for similar low-voltage applications. U.S. practice is to use lump containing 97 percent or more carbon, because it is known to perform satisfactorily under the severe operating conditions required. Substituting other grades would entail a prohibitive amount of bench testing of the end products to eliminate the risk of failure under operating conditions. The major strategic use for Malagasy flake graphite is in clay-graphite crucibles, which require coarse flake. Although the quantities needed are not large, these Ceylon amorphous lump and Malagasy flake graphites are important to domestic security and industrial activity.

The need for coarse flake graphite is decreasing, because crucible manufacturers are making silicon carbide-graphite crucibles in which the percentage of graphite is substantially less than in clay-graphite crucibles. One manufacturer has stated that silicon carbide-graphite crucibles require 18 to 25 percent graphite, compared with 45 to 50 percent for clay-graphite crucibles. Furthermore, much finer flake can be utilized. Domestic flake is said to perform satisfactorily and probably would be used if an assured supply could be obtained at a price comparable with that of Malagasy fine flake. Approximately 75 percent of the crucibles manufactured in the United States are silicon carbide-graphite crucibles. Complete substitution of silicon carbide-graphite crucibles for clay-graphite crucibles is unlikely; clay-graphite is used for special application, such as induction melting, and for large crucibles.

Manufactured-graphite shapes are used for electrodes, anodes, beams, blocks, brick, slabs, cylinders, metallurgical and chemical applications, bearings, bushings, nozzle and throat liners in jet engines, directional vanes in guided missiles, and moderators in atomic reactors. Manufactured-graphite powder is used in lubricants, brake lining, clutch facing, fabric belting, wire drawing, foundry facings, plastics, pigments, glass, dry-cell batteries, and other applications.

In Europe, large quantities of amorphous graphite are used in blast furnace charges to reduce the need for higher priced coke. The graphite is used as mined, without upgrading, for this purpose.

ALTERNATE MATERIALS

There is no satisfactory substitute for graphite in most applications. Some interchangeability is possible among all types and grades of natural graphite, and between natural and manufactured graphite, but the degree is difficult to determine. Because of its greater cost, manufactured graphite does not compete with natural graphite in most of its uses. On the other hand, natural graphite cannot be substituted for manufactured graphite in nuclear reactors because of the high neutron-absorption cross section of its usual impurities and because it is highly anisotropic and low in strength.

Manufactured graphite does not replace flake graphite in graphite-clay crucibles, although some crucibles are machined from manufactured graphite for special uses. The development of carbon-bonded silicon carbide-graphite crucibles (see "Uses") has reduced the quantity of

graphite needed for crucibles and the need for coarse flake. Other high-temperature refractory materials, such as the silicides, nitrides, and borides, may be suitable for uses now requiring graphite-clay crucibles.

RESERVES

Recoverable reserves of less than 5,000 tons of lump graphite occur in Montana with few veins having a strike length of as much as 50 feet. The veins range in thickness from less than 1 inch to about 2 feet; the quality of the graphite has not been determined.

No estimate of the amorphous graphite resource in Rhode Island is available, but it is very large.

Domestic deposits of crystalline flake graphite are low grade. Many of them contain less than 3 percent graphite, and most of them contain less than 5 percent; that is, they are about half the tenor of Malagasy ore. However, deposits in New York requiring underground mining, and others in Alabama, Pennsylvania, and Texas, which can be mined by open pit methods, contain a minimum of 600,000 tons of crystalline flake graphite. Only a small percentage is coarse flake that will meet specifications for crucible-grade graphite which must range from 8- to 60-mesh.

Quantitative data on reserves of amorphous and crystalline lump graphite in Ceylon are not available, but graphite veins cut igneous and metamorphic rocks in an area 95 miles long and about 40 miles wide in the southwestern part of the island. The veins range in thickness from less than an inch to several feet. Strike lengths range from a few to several hundred feet. Dips are nearly vertical, and some veins extend to a depth of at least 1,600 feet.

The reserve of amorphous graphite in Mexico is of the order of millions of tons. Large reserves also are known in Australia, Austria, the Republic of Korea, and the U.S.S.R.

The largest known reserve of flake graphite in the world is in the Malagasy Republic. Deposits occur in many individual districts throughout most of an area nearly 600 miles long and 100 miles wide. The graphite layers commonly are continuous for long distances; many can be traced for 3,000 to 4,000 feet along the strike. A few are up to 350 feet thick. Most of the commercial deposits are in the weathered outcrop of feldspathic gneisses, where tenor of the mined ore probably averages 5 to 6 percent graphite (*13*).

Large indicated reserves of crystalline flake reportedly occur in Australia, Austria, Brazil, Canada, China, West Germany, and Norway.

SOURCES OF STATISTICAL INFORMATION

Annual data on the production and shipments of natural graphite are obtained from domestic producers by the Bureau of Mines; annual data on consumption, by type of graphite and use, are obtained from consumers. No attempt is made to obtain detailed data from the many firms that consume less than 1,000 pounds per year. Some duplication results from reporting the same material as "processed for resale" by one establishment and "used" by another establishment. Frequently, consumers cannot identify the types and varieties of graphite in mixtures obtained from suppliers. However, the data collected are complete and accurate enough to be valuable in programing and mobilization planning. No data on stocks are published.

World production and trade data also are compiled by the Bureau from State Department dispatches and official publications of foreign countries, and U.S. exports and imports are obtained from the U.S. Department of Commerce.

PRODUCTION, CONSUMPTION, AND TRADE

World production of natural graphite, by countries, is given in table 1 for 1959–63, together with the 1954–58 average. It should be noted that the reported production for the Republic of Korea includes anthracite shipped to Japan and invoiced as amorphous graphite, presumably because of Japanese restrictions on imports of anthracite. Thus, it is doubtful that production of amorphous graphite from the Republic of Korea is much above its average output of 25,400 tons for 1949–53.

TABLE 1.—*World production of natural graphite, by countries*

[Short tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963
Austria	20,718	68,444	97,043	89,255	98,416	109,778
Ceylon	9,109	8,816	10,107	10,016	9,665	9,280
Germany, West	11,892	12,377	12,760	13,349	13,134	13,000
Korea, North [1]	23,003	57,000	68,000	72,000	72,000	77,000
Korea, Republic of [2]	89,674	91,045	101,777	98,892	204,032	334,777
Malagasy Republic	15,719	12,614	15,923	16,473	19,274	17,319
Mexico	27,302	30,684	37,827	19,846	31,992	33,000
Norway	5,344	5,396	6,437	6,283	7,055	7,000
U.S.S.R. [1]	45,000	50,000	50,000	55,000	60,000	60,000
Other countries [1 3]	57,500	73,600	75,000	69,000	74,500	69,000
Total [1]	305,000	410,000	475,000	450,000	590,000	730,000

[1] Estimate.
[2] Includes an unknown but large tonnage of anthracite reported as graphite.
[3] Includes Argentina, Australia, Brazil, Canada, Czechoslovakia, Hong Kong, India, Japan, Kenya, Morocco, Republic of South Africa, South-West Africa, Spain, Taiwan, Tanzania, and the United States.

The average U.S. consumption for 1959–63 was 8 percent higher than for the previous 5-year period. A large increase in the use of amorphous graphite for refractories was chiefly responsible for the greater consumption.

Ceylon, the Malagasy Republic, and Mexico provided 89 percent of the U.S. imports of natural graphite during 1959–63, with Mexico supplying 72 percent (table 3). The remainder was received from 12 other countries and Hong Kong.

The rate of duty in effect in December 1964, for import of crystalline flake, valued at not over 5.5 cents per pound, was 15 percent ad valorem; for flake valued at over 5.5 cents per pound, 0.825 cent per pound; for lump and chip, 5.5 percent ad varolem; for amorphous graphite valued at over $50 per ton, 0.5 percent ad valorem. For amorphous graphite valued at $50 per ton and under, duty was suspended until June 30, 1966.

TABLE 2.—*Consumption of natural graphite in the United States, 1959–63 (average), by types and uses*

Use	Ceylon amorphous and crystalline lump		Other amorphous [1]		Crystalline flake		Total	
	Short tons	Percent	Short tons	Percent	Short tons	Percent	Short tons	Percent
Batteries			928	3	58	1	986	3
Bearings	74	2	56	(2)	44	(2)	174	(2)
Brake lining	246	7	466	2	413	6	1,125	3
Carbon brushes	322	9	330	1	131	2	783	2
Crucibles, retorts, stoppers, sleeves, and nozzles	14	(2)		(2)	3,302	44	3,316	8
Foundry facings	486	13	13,496	46	540	7	14,522	36
Lubricants	1,809	48	2,268	8	1,672	22	5,749	14
Packings	25	(2)	195	(2)	229	3	449	1
Paints and polishes	43	1	364	1		(2)	407	1
Pencils	611	16	587	2	533	7	1,731	4
Refractories			4,073	14	65	1	4,138	10
Rubber	36	(2)	44	(2)	77	1	157	(2)
Steelmaking	80	2	6,288	21	234	3	6,602	16
Other [3]	58	2	461	2	253	3	772	2
Total	3,804	100	29,556	100	7,551	100	40,911	100

[1] Includes small quantity of mixtures of natural and manufactured graphite.
[2] Less than 1 percent.
[3] Includes adhesives, carbon resistors, catalyst manufacture, chemical equipment and processes, copper refining, electrodes, electronic products, fillers, insulation, plastics, powdered-metal parts, roofing granules, specialties, welding electrodes, and other uses not specified.

TABLE 3.—*U.S. imports and exports of natural graphite*

[Short tons]

Year	Imports for consumption						Exports
	Ceylon	Malagasy Republic	Mexico	Norway	Other countries	Total	
1954–58 (average)	3,201	5,899	26,774	1,570	3,668	41,112	1,154
1959	2,312	4,738	25,760	1,834	2,399	37,043	1,368
1960	2,836	3,465	36,913	1,637	3,288	48,139	1,855
1961	2,393	3,877	19,408	1,463	2,537	29,678	1,558
1962	2,811	5,108	22,519	2,106	2,345	34,889	1,159
1963	2,467	5,120	39,724	2,652	1,852	51,815	899

STRATEGIC CONSIDERATIONS

The United States has never been self-sufficient in any grade of graphite. Most amorphous and crystalline lump graphite are imported from Ceylon, virtually all crucible flake graphite from the Malagasy Republic, and all high-grade amorphous graphite from Mexico. Domestic production supplies only a small fraction of the peacetime needs. In case of an emergency, several low-grade deposits in the United States could be worked, but would require at least a year for development. The output from these domestic deposits, together with imported Mexican amorphous graphite, could achieve a measure of self-sufficiency for the United States. The cost, however, would be two to three times higher than the present market price of Malagasy flake. In addition, about 1,000 tons per year of Ceylon 97- to 98-percent carbon amorphous lump would be required for brushes in some motors and generators and other special uses.

GOVERNMENT PROGRAMS

Prior to World War II, the Government recognized that graphite from other sources could not be used efficiently for many purposes essential to military and civilian needs during wartime until new techniques of utilization could be established. As a result, certain grades of graphite deemed essential in wartime were designated as strategic and critical materials for stockpiling. Interim basic and maximum objectives were achieved for all strategic grades of graphite.

The stockpile program has been reevaluated in accordance with modern warfare needs. Many commodities were declared to be stocked in excess of requirements and a planned disposal was ordered. Certain grades of graphite were among those declared as excess stockpile materials, and an orderly disposal program was started in 1963.

Quantities of graphite in Government inventories are given in table 4.

The Office of Minerals Exploration, U.S. Department of the Interior, will participate in an exploration program for crucible flake graphite up to and including 50 percent of the approved cost.

TABLE 4.—*Graphite in Government inventories, June 30, 1964*

[Short tons]

	National (strategic stockpile)	DPA inventory	CCC stocks	Supplemental stockpile	Total
Ceylon amorphous lump	4,455			1,428	5,883
Malagasy crystalline	32,675			1,908	34,583
Other than Ceylon and Malagasy	4,809				4,809

PRICES

Oil, Paint and Drug Reporter, January 6, 1964, quoted prices for graphite as follows: Per pound, bags or fiber drums, exwarehouse, amorphous, powdered, 6 to 9.5 cents; crystalline, 88 to 90 percent, powdered, 19 to 21.5 cents; 90 to 92 percent, powdered, 21 to 24.5 cents; 95 to 97 percent, powdered, 29 to 31.5 cents; No. 1 flake, 90 to 95 percent, 29 to 31 cents; No. 2 flake, 90 to 95 percent, 29 to 31 cents. The prices quoted were unchanged from those published in 1958.

Prices quoted in E&MJ Metal and Mineral Markets, January 28, 1964, per metric ton, bags, f.o.b. source, except when otherwise noted, follow: Flake and crystalline graphite, Malagasy, $90 to $200; Norwegian, $80 to $140; German, $114 to $672; and Ceylon, per long ton, $95 to $250; amorphous, nonflake-cryptocrystalline, 80 to 85 percent carbon, Mexican, bulk, $17 to $20; Korean, bulk, $15; and Hong Kong, per long ton, $21. These prices show some changes from those quoted in 1958.

The quoted prices are only indicative of a range of prices between buyer and seller owing to the wide range of specifications. No prices are quoted for domestic production.

TAXES

Graphite producers are granted a depletion allowance for tax purposes of 23 percent on domestic production and 15 percent on foreign production.

RESEARCH

Research on natural graphite has not been extensive, but some efforts are continually directed toward improving methods of milling. A new flotation process for enriching amorphous graphite was recently developed and put to use in Austria (*3*). Research has developed new processes for using graphite in combination with various metals to form self-lubricating materials. Other new uses are occasionally developed, such as the use of amorphous graphite in European blast furnaces to replace part of the coke requirements.

Tests conducted by several manufacturers indicate that up to 10 percent domestic graphite could be mixed with Malagasy flake without greatly impairing the life of crucibles. Results from studies made by the National Bureau of Standards, U.S. Department of Commerce, indicate that domestic graphite of equivalent flake size and carbon content can be substituted entirely for Malagasy graphite without impairing crucible life (*5*, *6*, *8*). Past Bureau of Mines studies verify domestic flake of equivalent size and carbon content is equal to Malagasy flake.

Manufactured graphite has been the subject of substantial research both by industry and by Government agencies. Basic and applied research on oriented graphite is being conducted by an increasing number of firms with emphasis on missile and space vehicle applications. This stepped-up research on special graphite should lead to improved products, lower prices, and new uses. Several new types of special graphite lubricants have been developed, and research continues in this field. Another interesting area of research showing great promise for the future is the development of graphite fabrics.

Firms that have had a major role in the Government program to improve graphite, including pyrolytic graphite, are Union Carbide Corp., Carbon Products Division; General Electric Co., Hanford, Washington, and Schnectady, N.Y.; Lockheed Aircraft Corp., Palo Alto, Calif.; Raytheon Co., Waltham, Mass.; Bell Telephone Laboratories, New York, N.Y.; Atomics International (a division of North American Aviation), Canoga Park, Calif.; and Westinghouse Electric Co., Pittsburgh, Pa.

The U.S. Atomic Energy Commission continues its extensive research on manufactured graphite with respect to its uses in nuclear reactors.

In 1963, the American Society for Testing and Materials organized a committee, C–5, to promote knowledge, stimulate research, and develop test methods, specifications, and nomenclature for manufactured carbon and graphite products (*9*).

OUTLOOK

Both the short- and the long-term supply outlooks are favorable for graphite of all types required for the U.S. domestic economy. Output of all grades of Ceylon lump and Malagasy flake and fines is well below production capabilities, and producers in both countries are actively seeking additional markets. So long as supply lines remain open to Ceylon and the Malagasy Republic probably there will be no incentive for domestic consumers to attempt to develop alternate sources of supply, and the stockpile inventories will meet estimated essential wartime requirements even if no imports can be obtained.

The supply of domestic and Mexican graphite is ample, and productive capacity is greater than demand. Output undoubtedly will increase to meet the requirements of an expanding economy.

Graphite imports from sources other than Ceylon, the Malagasy Republic, and Mexico will be available on either a continuing or an intermittent basis; however, they are not essential, and other available types of graphite can be substituted for them.

There is no indication of a major increase in requirements for natural graphite. The shift to silicon carbide-graphite crucibles has reduced total requirements for crucible-flake graphite, and consumption of this type probably will not greatly exceed 4,000 tons a year. In a peacetime economy, the use of all other types of graphite in foundry facings, as a recarburizer in steelmaking, and for other applications will increase moderately.

New developments in manufacturing processes for graphite are important. The use of thermosetting plastics or furfuryl alcohol, to accelerate the graphitization of carbon, should increase. The method of producing oriented graphites by thermally decomposing hot carbonaceous gas on a hot substrate may lead to new or improved metallurgical applications in addition to space uses.

Special manufactured graphites that are denser, stronger, and more resistant to oxidation than conventional graphites are expected to find considerable use. Considerable interest has been generated in oriented and recrystallized graphites and present research may open new fields of use where their particular properties are required. However, the use of manufactured graphite in special applications, such as space vehicles and atomic reactors, is not likely to increase overall consumption greatly. Such uses receive spectacular publicity but they do not involve large quantities of materials.

PROBLEMS

A major problem of the natural-graphite-producing industry is the limited market for graphite of each type. Despite the fact that the free world prefers Ceylon and Malagasy graphite for most uses requiring high-quality graphite, producers in these countries must spend susbstantial effort attempting to widen their markets. This marketing problem is accentuated for other foreign and domestic producers.

Other sources of high-quality graphite usually cannot be exploited at a profit, because the demand is low and consumers are reluctant to change from satisfactory long-used sources to new sources that would require adjustments in formulas and manufacturing techniques, especially when there is no assurance of long-term continuing supplies from the new sources. Thus, even assuming that new producers could supply equal or superior grades of graphite at the same or lower prices than Ceylon and Malagasy Republic producers, their problem would remain one of marketing. Going concerns also face the difficulty of expanding markets for their products, because they are new to most potential customers.

Major technologic problems of the U.S. natural graphite industry are how to determine the degree of interchangeability possible among various types of graphite and among graphites of the same type from different sources, and how to reduce U.S. dependency on foreign sources of high-quality graphite, especially Malagasy crucible flake and Ceylon lump.

More reliable statistical information is required in order to properly evaluate the requirements, supply, and resources of the manufactured graphite industry.

A major fabrication problem of the manufactured graphite industry is to develop graphite with reproducibly constant properties for use as an engineering material. The variations in structure and properties within any single specimen or grade make present graphites unreliable for the severe service requirements in space applications.

Present emphasis has been on space-age applications of oriented and recrystallized graphites, but materials with such unusual strength and anisotropic properties must have other applications. Further research should develop less exotic but, perhaps more profitable uses.

The growth of whisker carbon and development of methods for testing all its properties alone and in combination with other materials is a problem worthy of more attention.

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GYPSUM

By William R. Barton [1]

PLASTER made from calcining gypsum (derived from the Greek words for "earth" and to "cook") is one of the oldest building materials in the world and its use continues to grow. Since 1890 the annual production of crude gypsum in the United States has increased 56.8 times, reaching 10.4 million short tons in 1963; while demand for gypsum products multiplied 95.0 times to 14.7 million short tons in 1963. The value of the products sold or used in the United States in 1963 was $414.1 million.

In 1963, a total of 71 mines and 68 calcining plants comprised the domestic (primary) gypsum industry. There were three major firms with nine or more calcining plants plus mines and quarries; nine other calciners, seven of whom also operated mines; and a number of small firms producing only crude gypsum for uncalcined uses.

Large deposits of gypsum occur in various parts of the United States. However, cheap water transport makes imported gypsum more economical for many tidewater gypsum product plants. In 1963, imports, mostly from Canada, were about one-third of the apparent domestic supply. Gypsum and gypsum products exports are of minor importance.

Gypsum consumption is closely related to fluctuations in the building construction field. As the Nation's population and concomitantly its requirements for buildings grows, the need for gypsum will increase. Domestic consumption of gypsum products in 1975 will probably exceed 20 million tons.

BACKGROUND

The early use of gysum was principally in art. Chinese, Assyrians, and early Greek sculptors and architects worked to some extent in this medium. The first verified use as a construction material was as mortar in the pyramid of Cheops about 3000 B.C. Its real importance, however, has been its value as a fire-resistant construction material. Records of Roman laws indicate early familiarity with the fact that if fire attacks a gypsum plaster wall, formation of steam from chemically combined water will consume heat and retard combustion, and the remaining mineral portion of the wall is nonflammable.

Early master chemists, including Lavoisier and Le Chatelier, investigated the composition and properties of gypsum, but the material was put to little practical use until late in the 18th century when it was utilized as a fertilizer and soil improver in Germany and France. Benjamin Franklin, when acting as the American Commissioner to France in 1776, became interested in the use of gypsum land plaster and the use of plaster as a fireproof wall finish, and introduced the use of the mineral to the United States.

Its application for soil improvement gained rapid acceptance in the United States. Initially, gypsum imported as ballast from France and Nova Scotia was used. The mineral was discovered in central New York in 1792 and subsequently in Virginia (1835), Michigan (1840), Ohio (1850), Iowa (1872), Colorado (1875), and California (1875).

The early production from these deposits was limited to localized use as fertilizer. The calcining of gypsum for use as a plaster began in New York about 1835, but it was not until the middle eighties that a commercial method to retard the setting of gypsum plaster was developed. This revolutionary discovery marked the true beginning of the gypsum industry by permitting practical use of plaster in construction. Coupled with the simultaneous growth of the portland cement industry, that required crude gypsum to control the "set" of the cement, an ever increasing demand was created.

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SIZE AND ORGANIZATION OF THE INDUSTRY

The U.S. gypsum industry has evolved to the point where most gypsum is mined and processed by large integrated manufacturers of building materials. A total of 71 mines and 68 calcining plants comprised the domestic industry in 1963.

The industry consisted of three major firms, each with nine or more calcining plants plus mines and quarries, nine other calciners, seven of whom also operate mines; and a number of small firms that produced gypsum or gypsite for cement retarder or agricultural purposes. The 10 large companies with mines accounted for 82 percent of U.S. crude gypsum output from 39 mines.

The United States Gypsum Co. is the principal producer of both crude and calcined gypsum. In 1963, this organization operated 13 mines or quarries in 13 States and 25 calcining plants in 17 States. National Gypsum Co. operated 7 mines or quarries in 7 States and 17 calcining plants in 16 States. Bestwall Gypsum Co. operated six mines or quarries in six States and nine calcining plants in nine States. United States Gypsum Co., National Gypsum Co., Kaiser Gypsum Co., and the Flintkote Co., operated large mines in Nova Scotia or Newfoundland, and United States Gypsum Co. operated mines in Mexico and Jamaica as well. In addition, new plants are planned for Georgia, Texas, Nevada, Arkansas, Montana, Florida, New Jersey, California, and Oklahoma.

The United States is the world's largest producer and consumer of gypsum, producing about one-fifth of the world's crude gypsum and consuming almost one-third of the world output.

The quantitative growth of the gypsum industry in the United States since 1890 can be visualized by realizing that by 1963 domestic crude production had increased 56.8 times and domestic consumption of gypsum and gypsum products had multiplied 95 times.

GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

In 1963 there were 71 active gypsum mines in 21 States. The leading producer was California with 17 percent of all raw gypsum mined, followed by Michigan, 13 percent; Iowa, 12 percent; and Texas, 11 percent. Fifty-five of the mines were open-pit and 16 were underground. Seventy-five percent of the Texas crude, 70 percent of the Iowa crude, and 28 percent of the Michigan crude were calcined within those States. Forty percent of the California production was sold uncalcined for agricultural use.

The calcining component of the domestic industry was represented by 68 plants in 29 States. The leading calcining States were New York (seven plants), California (six plants), Texas (six plants), and Iowa (five plants).

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

The American Society for Testing and Materials has established specifications for gypsum and gypsum products.[2] They are too voluminous to quote in this report, but have been used in part to help promulgate the following definitions and are listed by number wherever applicable.

Gypsum, is the generic name for the mineral (hydrous calcium sulfate, $CaSO_4 \cdot 2H_2O$) variously known as selenite, a transparent cleavable form usually colorless; satin spar, a fibrous form with a silky luster; alabaster, a massive fine-grained variety, usually white and translucent; rock gypsum, a compact, granular form, coarser grained than alabaster; and gypsite, a soft, earthy impure form, noncoherent to slightly consolidated. In its pure state, gypsum is composed of 32.5 percent lime (CaO) 46.6 percent sulfur trioxide (SO_3), and 20.9 percent water. The importance of gypsum lies in its ability to lose three-fourths of its combined water upon application of moderate heat (between 250° and 400° F.) to form a hemihydrate. And its further ability, in hemihydrate form, to be molded upon addition of water, followed by a return to its rigid state upon "setting" (ASTM Specification C–22–50).

To obtain ultimate strength, lightweight aggregate carrying capacity, and other characteristics desirable in wallboard cores and plasters, companies prefer to use ore containing not less than 90 percent gypsum. Ordinarily, a gypsum deposit to be considered commercial and meet competition should have minable beds containing at least 80 percent gypsum. Color, density, and other factors also may be considered. Lower grade ores may be upgraded through use of heavy medium process to meet competition from other sources. In certain markets, such as soil conditioning, specifications often permit use of material containing as low as 50 percent calcium sulfate.

Anhydrite is an anhydrous calcium sulfate mineral ($CaSO_4$) usually massive and white or slightly colored. In its pure state, it is composed of 41.2 percent calcium oxide and 58.8 percent sulfur trioxide.

[2] Copies of specifications can be obtained from the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pa., for 50 cents each.

Land plaster, agricultural gypsum, is gypsum or gypsite used as a soil conditioner.

Calcined Gypsum ($CaSO_4 \cdot \frac{1}{2}H_2O$) is gypsum partially dehydrated by heating to between 250° and 400° F. This material is more popularly known as *Plaster of Paris* and is also called *Gypsum Hemihydrate* (ASTM Specification C–28–63 and C–59–50).

Dead-burned gypsum is gypsum completely dehydrated by calcining at 900° to 1,100° F. It is sometimes called *anhydrite* since its chemical composition is the same as the naturally occurring mineral.

Keene's Cement is dead-burned gypsum to which the property of quick setting has been restored by using certain salts. It has a hard finish and will take a polish. It is often used for ornamental plaster work (ASTM Specification C–61–50).

Accelerators are materials added to gypsum plaster to speed up natural set.

Retarders are materials added to gypsum plaster to slow up its natural set.

Gypsum board consists of a gypsum plaster core between paper outside layers.

Wallboard is used for walls and ceilings and is fastened directly on wood or metal framing or furring strips. The most popular thicknesses are, ⅜ inch, ½ inch, and ⅝ inch in standard 4 foot widths and various lengths (ASTM Specification C–36–62).

Gypsum Sheathing is water repellent, windtight board used for exterior sheathing without covering by building paper. It has a special water resistant paper incorporated as an outer layer and comes with tongue and groove edges. Its usual dimensions are ½ inch by 2 feet by 8 feet or ½ inch by 4 feet by 8 feet (ASTM Specification C–79–54).

Lath used as a plaster base is similar in construction to wallboard but is generally 16 inches by 4 feet and usually ¾ inch thick. It can be obtained with or without perforations or aluminum foil backing (ASTM Specification C–37–54). Several other forms including ceiling tile and laminated varieties are also sold.

Reinforced gypsum concrete is usually precast. It consists of calcined gypsum mixed generally with up to 12½ percent by weight of wood fiber, chips, or shavings and reinforced with steel bars or wire (ASTM Specification C–277–63).

TECHNOLOGY

Geology

Gypsum is abundant and widespread in the United States. Gypsum and anhydrite normally occur as sedimentary strata precipitated from saline waters, but occasionally they are found as a precipitate resulting from the chemical action of sulfuric acid and sulfates upon lime-bearing minerals, by the surficial disintegration and reaccumulation of pre-existing sediments as gypsum dunes, or as gangue minerals in ore deposits. The primary sequence of gypsum and anhydrite in sedimentary strata is determined by their order of precipitation as brine evaporates, the general sequence of major evaporite units being limestone, gypsum, anhydrite, salt, polyhalite with varying repetitions and omissions of strata being the rule rather than the exception. However, the present geological relationship of gypsum to anhydrite is largely secondary and is closely correlated with their depth below the surface. Gypsum preponderates in near-surface deposits, and anhydrite predominates at depths. This is generally attributed to the alteration of original anhydrite to gypsum by percolating ground waters close to the surface. The depth of alteration is affected by porosity and permeability of the strata and present and past water table positions. In New York, for example, alteration generally extends to a depth of 110 to 250 feet below the surface. In the United States gypsum beds rarely exceed 30 or 40 feet in thickness, but in the Canadian maritimes beds 40 to 100 feet thick are not uncommon. Common impurities are intercalated limestone and shale, clay, and sand. Because of their sedimentary mode of origin, deposits usually have wide lateral extent.

Mining

Most domestic gypsum is mined by open-pit methods. Underground mining is confined to deposits where the increased costs are compensated by higher quality ore, or proximity to the market.

The mining method selected to develop any particular deposit depends largely on the depth and composition of the overburden and the thickness and attitude of the gypsum deposit. The overburden may consist of glacial till, sand, gravel, alluvium, clay, limestone, shale, or other material. Overburden is removed by conventional earth moving equipment. In stripping, bank slopes are usually maintained at a $1\frac{1}{2}:1$ ratio. The number and width of berms or benches left during stripping are dependent on the depth of the ore from the surface. Stripping of the ore may become complicated if the surface of the deposit was exposed, prior to glaciation, to a weathering cycle which permitted portions of the deposit to be deeply dissected. The uneveness of this surface formed by action of the elements may present problems of contamination and in surface drilling. Maximum stripping ratio of waste to gypsum is

about 3:1, but in Canada 1:1 or even 1½:1 is the more common ratio.

In open-pit mines the blasting agents used are either ammonium nitrate-fuel oil or medium strength dynamite. In large open pits ore is loaded almost exclusively with power shovels, but in some thin bedded deposits it may be loaded with dragline excavators. The height of the benches generally ranges from 10 to 30 feet. Ore is transported from the pits by trucks, skips, trams, conveyor belts, or by combinations thereof. In mining, impurities (commonly shale, limestone, clay, or anhydrite) must be left, sorted out, or low-grade ore selectively removed to avoid contaminating the higher grade material preferred in the manufacture of calcined gypsum products. Often anydrite cannot be recognized easily, and careful sampling must be done to permit selective mining of gypsum.

Drainage problems are similar in most operations. Rain water and ground water are directed by ditches to strategically located sumps where the water is collected before being pumped from the pit and discharged into natural drainage features.

The room-and-pillar method is usually used when mining flat-lying gypsum deposits underground. Pillars range in size according to the condition of the roof and the thickness of the deposit. Under good conditions, 80 percent of the gypsum is recovered, but in sections of bad ground and weak roofs, larger pillars are left for adequate support. Where gypsum is not left as a roof or where the pillars can be drawn and the surface is allowed to cave, a deposit may be completely mined out. Roof bolts and timber may be used to strengthen slabbing roofs and areas weakened by solution cavities. Both percussion and auger drills are used in underground mines. The ore is broken by a medium-to-high velocity explosive detonated by conventional cap and fuse or by electricity. Broken ore is loaded and is transported underground by conventional methods. If beds are steeply dipping, drifting and shrinkage stoping are the mining technique normally used.

Beneficiation

Crushing operations at a gypsum mill consist essentially of two stages. The first may employ gyratory or jaw crushers, and the second hammer mills or roll crushers. Jaw or gyratory crushers reduce the crude ore as it comes from the pit to minus 3-inch size. The second stage crushers reduce the ore to minus ½-inch size, which provides a suitable feed for the rotary kiln or the grinding circuit.

Fine grinding is accomplished by tube and hammer mills, rolls, or other pulverizing equipment, either before or after calcination, depending upon the calcination process used.

The large quantity of high-grade gypsum available has discouraged any serious attempt to beneficate low-grade gypsum ore by flotation or gravity methods. Heavy medium separation equipment is used in a few localities for the beneficiation of gypsum ores. For efficient operation the feed must be thoroughly screened and washed to remove all fines. Beneficiation of gypsum may be effected by using a drum separator that employs a mixture of finely ground magnetite and ferrosilicon as the heavy medium. Heavy medium used in the process may be reclaimed from the sink and float products through the use of rinsing screens, drum electromagnetic separators, densifiers, and demagnetizing coils.

A method for flotation of silica from gypsum is used if silica free gypsum is required for glass or ceramic use (*1*).[3]

Processing of land plaster, gypsum cement retarder, fillers, or for other end uses requiring uncalcined gypsum, includes only crushing and grinding followed only by screening and classification.

Calcining

Calcining is the process of partly or completely dehydrating gypsum through the application of heat in gypsum kettles, rotary kilns, or under steam pressure in autoclaves. When kettles are used the gypsum must be ground before being calcined, but when a rotary kiln is used fine grinding is not required before calcination. Open pan and beehive, oven, or tunnel kilns are rarely used, particularly in the United States.

The properties generally desired in calcined gypsum include the following: High tensile and compressive strength, hardness, fineness of grind, and uniform setting time. Certain other properties are more essential for some applications of calcined gypsum than others. Plasticity is highly essential in hair-fibered wall plaster intended for use with aggregates. This property is not so important when calcined gypsum is used in manufacturing prefabricated products, such as wallboard and tile. The demand for plasticity also varies with the sand used in wall plasters, the lack of plasticity with a given amount and kind of sand can cause the mortar to work short. Mortar having an excess of plasticity is as objectionable as mortars that work short.

Kettle calcining is done with batches ranging from 10 to 20 tons per kettle. Ground gypsum is fed through charging doors into kettles

[3] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

heated to 212° F. For 1 to 4 hours the charge is continuously stirred while temperature is gradually increased to 340° or 390° F, and then the material is discharged through a gate into cooling bins, each large enough to hold the contents of one kettle. Usually the kettles are emptied completely in 2 minutes as hot calcined gypsum flows freely. Between 30 minutes to 1 hour after the kettles are discharged, the material is removed from the cooling bins by conveyors and elevators and is transported to storage bins. In gypsum calcined in kettles, two distinct products are recognized, depending on the temperature reached during the process. The first and most important of the two products is "first settle" calcined gypsum drawn when the temperature reaches 325° to 340° F. It consists largely of the hemihydrate ($2CaSO_4 \cdot H_2O$) containing 5 to 6 percent water. The time required to calcine a kettle of raw gypsum to "first settle" material ranges from 1 to 3 hours, depending chiefly on the rate of firing, the fineness and purity of the raw material, and the kettle size and design. The second product is "second settle" calcined gypsum obtained by heating the kettle contents beyond the first settle stage to about 390° F. The "second settle" material consists chiefly of soluble anhydrite, which reverts to the hemihydrate on exposure to air. This material sets quickly, has higher tensile and compressive strengths, and is less plastic than the gypsum heated to 325° to 340° F. This material is also entirely different from the dead-burned gypsum formed by prolonged calcining at over 400° F.

Rotary kilns similar to those used by the portland-cement and lime industries are used for the calcining of crude gypsum. The kiln consists essentially of a slowly revolving cylinder inclined slightly from the horizontal, through which rock passes downward and is calcined to 325° to 340° F. by hot gases flowing counter to the flow of the rock. Kilns range in length from 70 to 155 feet and have diameters from 6 to 8 feet. Rock gypsum screened to ½-inch size is fed into the kiln at the high end. Passing through the kiln in about 45 minutes, the material is discharged directly into tube mills where the temperature attained by friction and impact is sufficient to calcine any unburned material. Overburning or underburning is prevented through the use of automatic controls which govern the temperature and rate of travel of material through the kiln. Advantages claimed for this kiln include high capacity, low labor costs, and relatively low fuel and power requirements.

Special plasters may be prepared in closed cylinders or autoclaves under steam pressure. No agitation is required, and as the temperature rises the water of crystallization is released and the hemihydrate is formed at about 250° F. The calcine produced by this method consists of particles that appear as short, broad base, dense crystals that possess properties different from other plasters. Less mixing water is needed to produce a smooth-flowing plaster with this material than required with ordinary plasters. When set, the plasters form a remarkably strong and dense product, useful wherever a product of superior quality is required.

Product Preparation

After calcination regrinding, mixing and blending prepares the gypsum plaster for use. If the plaster was produced in a kettle, grinding is not required, the product instead is simply passed over a vibrating screen. It is then mixed and blended with accelerators or retarders and any filler or binder required.

The setting time of calcined gypsum used in prefabricated products generally is accelerated. On the other hand, a retarder is used almost always in manufacturing wall plasters to control the time of setting to between 2 and 6 hours. Wall plaster is made by tube-milling calcined plaster of paris to very fine particle size. This material is thoroughly mixed with the retarder, fiber, and perhaps small quantities of other materials.

A great many substances have been used to retard or accelerate the set of calcined gypsum plasters. The action of these substances appears to be mechanical in that they hinder or help the crystallization of the calcined gypsum. Retarders are usually dispersing or deflocculating agents, whereas accelerators are coagulating or settling agents. Organic materials such as glue, gylcerin, flour, blood, and sugar are commonly used as retarders. In the United States the most commonly used retarder is a glue prepared by reducing hoof meal or low grades of hair with caustic soda. Potassium sulfate, alum, gypsum, or common salt may be used to accelerate the set of gypsum plasters.

Common admixed fillers and binders include asbestos, sand, sisal, sawdust and cork. If lightweight plaster or tile is to be the product, vermiculite or perlite are generally added. Sheet products are fabricated on a high-speed machine that automatically spreads a foamy plaster core between sheets of tough surface papers and cuts the resultant board to proper dimensions.

USES

The most important, and continually expanding, market for gypsum is the construction industry, especially in housing. Basecoat,

finish and acoustical plasters, wallboard, lath, sheathing, laminated, other board products, and ceiling tiles are the principal forms. The wide utility of these products is indicated in table 2. Prefabricated forms have been taking a continually increasing share of the construction market from wet plaster but due to market expansion total volume of both varieties has increased.

Gypsum has many uses in addition to those in construction. Three to 6 percent by weight of gypsum or anhydrite is added to cement clinker before it is ground. This quantity of gypsum or anhydrite in finished cement retards the setting and is an essential part of this important construction material. Ground gypsum is used on soils deficient in sulfate sulfur and as a soil conditioner. Applied to black alkali soils it transforms the sodium carbonate into calcium carbonate and sodium sulfate. It is also used in Europe for the fixation of volatile nitrogen in manure, converting the ammonium carbonate into ammonium sulfate.

An important market for calcined gypsum is for making models and patterns in industrial tooling activities. There are particularly heavy requirements in the aircraft and automotive industry. Calcined gypsum is used for the manufacture of molds. Requirements for this material include absorption of moisture from slip, sufficient strength, and that pitting of the mold must be retarded.

Pastel crayons or chalk utilize calcined gypsum in their composition. Small amounts of calcined gypsum are used in mixtures as an insulating filler between the walls of safes and filing cabinets and coverings for pipes and boilers. Calcined gypsum is used in surgery for orthopedic bandages and for plaster casts. When used in orthopedics, open-mesh bandages are impregnated with finely-ground calcined gypsum and rolled until ready for use. Calcined gypsum with especial retardation is employed in making casts of dental work. Ceiling and wall embellishments are made from calcined gypsum to which hemp fiber has been added. Calcined gypsum also is used in the casting of Babbit and other metals.

Calcined gypsum has many minor uses: Preparation of casts and protecting fossil remains during removal to museums; briquetting of coal; as a dehydrating agent; as a filler in paper and other products; as a setting for gold, silver, and stones for engraving and polishing; and in numerous articles such as facial powder, dental powder, etc.

Calcium sulfate is added in small quantities to water used by the brewing industry to promote enzyme action, assist in yeast fermentation, and to clarify the liquid.

Calcium sulfide is formed when an intimate mixture of ground gypsum and coke or charcoal is burned under reducing conditions. Calcium sulfide is used in the manufacture of medicine, luminous paint, and hydrogen sulfide; and as a base for calcium lithopone, insecticide, and fungicide.

Dead-burned gypsum finds use as a desicator and to dehydrate, or remove moisture, from gases.

Gypsum may be used as a substitute for sodium sulfate in a glass batch. It is claimed that the evolution of the combined water assists in clearing the glass melt. Gypsum plaster also is used by the glass industry for leveling up and holding the glass to the polishing table in the grinding and polishing of plate glass. This application faces a decline due to a technical change in plateglass production. The new "float glass" process involves the cooling of molten glass on a bed of molten metal, which produces a smooth surface without polishing and thus eliminating the need for gypsum in this application.

Fillers for use in wood, paints, textiles, and paper are made with gypsum or dead-burned gypsum. One of the principal uses of anhydrite is in the manufacture of ammonium sulfate. Used mainly in Europe, the process may be briefly described as follows: A solution of 25 percent ammonia is reacted with carbon dioxide forming ammonium carbonate, which in turn reacts with finely ground anhydrite, producing ammonium sulfate in solution and solid calcium carbonate. The ammonium sulfate is then recovered by filtration, crystallization, and drying.

The possibility of using gypsum or anhydrite as a raw material from which to manufacture sulfuric acid has attracted much attention because of the technical and commercial success achieved in Europe. Several chemical processes for accomplishing this have been tried; currently the most favored in England is that of calcining gypsum or anhydrite at high temperatures along with coke, silica, and clay, from which SO_2 and SO_3 gases (and a portland cement residue) result. These two gases then are converted to sulfuric acid.

Because of large alternative sources of sulfur, gypsum and anhydrite are considered to be uneconomical sources of sulfur in the United States; but if better methods are discovered or sulfur prices increase sufficiently, a new market for large-tonnage use of raw gypsum would be opened.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Three tons of byproduct gypsum remain as residue for every ton of phosphoric acid made

during the production of superphosphate fertilizers from rock phosphate. In the United States, some of these residues are used for soil dressing, principally on tobacco fields. The waste material contains up to 10 percent residual acid and would require special treatment to make it suitable for other use. For most U.S. residues the cost of special treatment would exceed the cost of mining rock gypsum. A few piles of residue containing less acid than ordinary are reported to exist in this country. In Japan some residues of this type are reclaimed and used in the manufacture of plaster and wallboard, as cement retarder and for land plaster.

Byproduct gypsum also results in industrial processes when a calcium salt is neutralized by sulfuric acid and during the recovery of salt from sea water by evaporation. These gypsum residues are not used because of the exorbitant costs of purification except for gypsum recovered at a salt works in Taiwan for use in cement. As previously noted, when sulfuric acid is made from gypsum or anhydrite in Europe, byproduct portland cement or lime is marketed. This process is not used commercially to produce sulfuric acid in this country, but the Bureau of Mines has described one method of making sulfur dioxide and cement from gypsum in a fluidized-bed reactor (*7*).

ALTERNATE MATERIALS

Lime and hydraulic cement plasters compete to a limited extent with gypsum in the plaster field.

Wood, plastics, organic fibers, aluminum, and glass used for inside finishing compete directly with gypsum lath, wallboard, and sheathing.

Cement retarders such as calcium chloride, sugar, and certain other organic substances have occasionally been used but have not become serious competitors of gypsum.

Anhydrite is used to a relatively small extent for land plaster and cement retarder in the United States. It could also be used as a gypsum substitute in many other ways if gypsum suppliers in the United States were unable to meet demands (which is not likely in the forseeable future). In Europe anhydrite is used in making ammonium sulfate and, as mentioned before, is decomposed to make sulfuric acid and cement.

RESERVES

Gypsum deposits of good quality occur in many States. All of the States in the Rocky Mountain area have substantial deposits. Extensive deposits also are known in the western States of California, Kansas, Nevada, Oklahoma, and Texas. In the Midwest, Iowa, Indiana, Michigan, and Ohio are the principal sources; and in the East, New York and Virginia. No sizeable commercial deposits have been found in Wisconsin, Minnesota, northern California, the Pacific Northwest, the deep South east of Louisiana, or New England (*14*).

The measured resource of gypsum in the United States has been estimated to be sufficient to provide 2,000 years of output at present rates. Additional major reserves are available to U.S. consumers from Canada, Mexico, and the Caribbean Islands.

Anhydrite and phosphoric acid plant residues constitute additional latent resources if they are ever needed or become profitable to work.

So many regions throughout the world are endowed with gypsum desposits, that consumer nations are able to obtain the major part of their requirements from local sources. The world resources have been well described by the British Overseas Geological Survey's Division of Mineral Resources (*3*).

SOURCES OF STATISTICAL INFORMATION

Annual and quarterly data on the production, sales, and stocks of gypsum products are obtained from producers by the Bureau of Mines. World production data are compiled by the Bureau of Mines from foreign service dispatches and official publications of foreign countries, and figures on foreign trade are obtained from the Bureau of the Census. The Bureau of Mines publishes quarterly Mineral Industry Surveys on Gypsum and a comprehensive annual report is included as a chapter in Minerals Yearbook.

The Department of Commerce publishes Construction Review monthly which includes statistics on the utilization of gypsum products in the construction field.

PRODUCTION, CONSUMPTION, AND TRADE

Domestic crude gypsum production and consumption of gypsum products, during selected years, 1890 through 1963, is given in Table 1.

The United States in 1963 contributed about 19 percent of the total world production of 54 million tons of crude gypsum (a declining share at approximate constant volume). Table 2 shows the production and value of gypsum products sold or used in the United States in 1962 and 1963.

The value of all gypsum products sold in the United States in 1963 was $414.1 million and weighed approximately 14.7 million tons.

TABLE 1.—*Historical growth of the gypsum industry in the United States, for selective years, 1890 through 1963*

Year	Crude gypsum production (thousand short tons)	Gypsum products sold or used					
		Uncalcined except land plaster		Land plaster		Calcined	
		Thousand short tons	Value per ton	Thousand short tons	Value per ton	Thousand short tons	Value per ton
1890	183	19	$1.02	57	$2.53	79	$5.20
1919	2,420	470	2.83	40	4.64	1,596	8.90
1929	5,016	1,028	1.88	38	4.23	3,362	8.69
1939	3,227	793	1.97	75	4.86	3,224	13.65
1949	6,608	1,564	3.41	426	4.20	6,359	23.84
1959	10,900	2,801	4.44	1,188	3.09	10,657	34.93
1963	10,388	2,947	4.58	1,262	3.46	10,519	37.67

TABLE 2.—*Gypsum products (made from domestic, imported, and byproduct crude gypsum) sold or used in the United States, by uses*

[Thousand short tons and thousand dollars]

Use	1962		1963	
	Quantity	Value	Quantity	Value
Uncalcined:				
Portland-cement retarded	2,765	$12,365	2,898	$12,931
Agricultural gypsum	1,241	4,222	1,262	4,372
Other uses [1]	43	510	49	562
Total	4,049	17,097	4,209	17,865
Calcined:				
Industrial:				
Plate-glass and terra-cotta plasters	43	714	46	776
Pottery plasters	48	1,073	50	1,115
Dental and orthopedic plasters	13	487	13	484
Industrial molding, art, and casting plasters	85	1,806	90	1,945
Other industrial uses [2]	80	2,665	80	2,774
Total	269	6,745	279	7,094
Building:				
Plasters:				
Base-coat	1,026	18,294	1,036	19,158
Sanded and premixed perlite	504	12,247	477	11,837
To mixing plants	1	16	1	21
Gaging and molding	119	2,521	123	2,649
Prepared finishes	10	869	9	821
Roof-deck	344	5,186	325	4,622
Other [3]	16	997	19	1,033
Keene's cement	35	924	36	963
Total	2,055	41,054	2,026	41,104
Prefabricated products [4]	[5] 7,711	327,404	[5] 8,214	348,027
Total		368,458		389,131
Grand total, value		392,300		414,090

[1] Includes uncalcined gypsum for use as filler and rock dust, in brewer's fixe, in color manufacture, and for unspecified uses.
[2] Includes dead-burned filler, granite polishing, and miscellaneous uses.
[3] Includes joint filler, patching, painter's, insulating, and unclassified building plasters.
[4] Excludes tile.
[5] Includes weight of paper, metal, or other materials.

Consumption, as measured by gypsum sold or used, is closely tied to general construction activity.

Most gypsum imports (table 3) are from Nova Scotia and are shipped by low-cost water transportation into the New England and Atlantic Coast States, while smaller but locally important tonnages are imported from San Marcos Island in the Gulf of Lower California (Mexico), Jamaica, and the Dominican Republic through ports on the Pacific coast and Gulf coast. Foreign ores, most of which are produced by subsidiaries of U.S. companies, account for approximately one-third of the apparent domestic supply.

TABLE 3.—*U.S. imports for consumption of crude gypsum (including anhydrite), by countries*

[Thousand short tons and thousand dollars]

Country	1962		1963	
	Quantity	Value	Quantity	Value
North America:				
Canada	4,086	$7,473	4,400	$8,714
Dominican Republic	453	1,240	26	77
Jamaica	283	1,052	169	508
Mexico	599	725	891	1,577
Total	5,421	10,490	5,486	10,876
Europe:				
France			4	10
Italy	(1)	(2)	(1)	1
Total	(1)	(2)	4	11
Grand total	5,421	10,490	5,490	10,887

[1] Less than 1,000 tons.
[2] Less than $1,000.

Source: Bureau of the Census.

Exports are a very small portion of total sales, and a breakdown by country of destination is not made.

The United States does not levy a tariff on crude gypsum. Imports of ground or calcined gypsum are subject to a duty of $1.06 per short ton ($1.25 if from Communist nations). Gypsum board products are charged 12½ percent ad valorem.

STRATEGIC CONSIDERATIONS

Although the United States has adequate reserves of gypsum, the deposits are unevenly distributed throughout the Nation. Regional shortages exist, and consequently it is cheaper to import ore to serve major markets in the Atlantic, Gulf, and northern Pacific coastal areas.

The overseas sources could be disrupted by submarine activity in wartime and might require expansion of the domestic mining industry. However, during a war nonessential home construction would be restricted thus lowering the demand from gypsum products and concomitantly lowering ore requirements.

The calcining industry is sufficiently dispersed so that only a general nuclear holocaust could cause serious dislocations.

GOVERNMENT PROGRAMS

During World War II, the War Production Board sharply curtailed public and private construction, thus limiting the production of gypsum in most parts of the country. On the other hand, since the war the gypsum industry has benefited from government programs that have encouraged building construction.

The Area Redevelopment Administration program for depressed areas includes consideration of possibilities for gypsum mines and calcining plants as means of stimulating the economic growth of such localities.

PRICES AND COSTS

The average value of domestically produced crude gypsum has increased from $2.77 per short ton in 1949 to $3.67 in 1963. For imported ore the increase has been from $1.04 to $1.98 per short ton. The higher average values for the United States product are due to higher average mining costs (some of the U.S. mines are underground while foreign sources are almost entirely open-pit). U.S. mines are further handicapped by higher-cost rail shipment to plants compared with foreign mines shipping by water transport to U.S. seaboard calcining plants. Open-pit mining is preferred whenever possible to underground mining due to higher efficiencies per man and machine, lower development, and lower total operating costs. Some foreign open-pit mine costs are reputed to be only one-third those in some U.S. underground operations. A striking example of the effect of comparative mining and shipping costs, is that Nova Scotia open-pit mines can ship rock gypsum into the New York City area cheaper than underground mines in New York State. Values of imported versus domestic rock gypsum for selected years 1929 through 1963 are presented in table 4.

TABLE 4.—*Average values reported for crude gypsum mined in the United States and for imported crude gypsum, selected years 1929 through 1963*

[Per short ton]

Year	Domestic	Imported	Year	Domestic	Imported
1929	$1.97	$1.02	1959	$3.59	$1.93
1939	1.37	.90	1963	3.67	1.98
1949	2.77	1.04			

Values of gypsum products made from domestic, imported, and byproduct gypsum sold or used in the United States in 1962 and 1963 by users are shown in table 2.

TAXES

The U.S. income tax law grants domestic producers a depletion allowance of 15 percent of gross income from domestic and foreign crude production.

TRANSPORTATION

Transportation is a large factor in the economics of the gypsum industry. Gypsum ore and finished products are heavy, bulky, and relatively expensive to move; consequently product plants should be near the mine and the market area. A nearly ideal relationship of mine and plant to consuming areas exists in some areas, whereas in others, especially in the Western States and along the east coast, either the crude ore or the finished product or both must be shipped considerable distances. In some instances plants have been established in a consuming area and supplied with crude ore by water transportation.

RESEARCH

Leading firms of the gypsum industry maintain research laboratories and engineering staffs to improve methods of mining, crushing, calcining, and end-product manufacture.

Some long-range studies now in progress in industry relate to the chemistry of the material and seek to determine methods of application productive of maximum usefulness. These include studies of the general problem of adhesion of calcium sulfate plasters to other materials; studies of aggregates problems; studies of the effect of gypsum (retarder) content on comprehensive strengths of concretes; and studies of compressive strength of plasters mixed and applied under varying conditions by various methods.

Thermodynamic properties of gypsum and gypsum plaster were studied by the Bureau of Mines (*4*). Hydration rates were also studied (*2*).

The Gypsum Association and the Acoustical Materials Association study properties, specifications, and methods of using gypsum-bearing architectural materials.

OUTLOOK

The outlook for the gypsum industry is one of continued, long-term growth as the Nation's economy expands. Since World War II the industry has been characterized by expanding use of prefabricated gypsum products in preference to other building materials. This expansion, which is expected to continue, can be attributed to good insulating and fire-resistant properties, wide range of hardness and density, and an increasing need for less expensive rapid methods of construction. Other factors which are expected to sustain increasing gypsum output are—(1) the increase in the number of families; (2) Federal, State, and municipal programs of highway construction and slum clearance; (3) replacement of substandard housing; (4) the availability of funds for low-cost mortgages, and (5) the projected annual increase in gross national product.

Future demand for gypsum and gypsum products may be projected against consumption increases since World War II, projected future population growth (1.6 percent compounded annually), and projected increase in gross national product (3.8 percent compounded annually), and projected rise in the construction component of the GNP (4.8 percent compounded annually). Using these four methods, U.S. consumption of gypsum and gypsum products in 1975 would be 20 million, 17.7 million, 23 million, and 25.8 million, respectively. The last projection would probably be high owing to possible increased use of substitutes. However, consumption of more than 20 million tons in 1975 seems reasonable. Most of the increase will be supplied by processing imported ores at seaboard plants (many presently under construction or planned) with lesser increases in domestic ore production.

The continual development of new forms and variations of gypsum products for use in the building industry has fostered the growth of gypsum consumption in that field. However, continued competition will be experienced from alternative materials in the future, restraining the growth rate to some extent.

These competitor materials include wood, plastics, organic fibers, aluminum and glass, and they compete directly with gypsum plaster, lath, wallboard, and tile for inside finishing and with gypsum sheathing for exteriors. Gypsum, however, has an intrinsic advantage over some of these competitors in its fire resistant and retardent properties.

The growing factory-built concept for both housing and business room modules and complete homes has turned largely to nongypsum materials at present for finishing purposes, and if this industry increases its share of the construction market it may restrain demand increases for gypsum products.

The reserve situation will probably change comparatively little for many years. As reserves providing raw material to some plants become depleted, other sources may replace them if adequate prospecting programs are maintained. The United States will continue to rely on foreign sources for a portion of its crude gypsum needs; probably an increasing share owing to lower production costs and economical water transportation to U.S. seaboard processing plants.

There is only a slight prospect of gypsum or anhydrite being used as a raw material for producing sulfuric acid in the United States. The costs of using known processes are still too high to compete economically.

Some residue piles at phosphoric acid plants will find utilization at least for soil conditioner purposes.

PROBLEMS

There is a local problem of crude supply in areas far removed from deposits of commercial significance or in areas where the rate of depletion exceeds new resources being developed.

Lack of geographical and other commodity detail on gypsum products limits understanding of the structure and trends of the industry.

Expensive processing compared with alternate raw materials, blocks the use of gypsum as a raw material for the manufacture of sulfuric acid.

Competition from new construction materials, such as plastics for interior finishes, may intensify.

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HAFNIUM

By Donald E. Eilertsen [1]

HAFNIUM, discovered in 1922 and available commercially for the first time during the last decade, has quickly assumed an important role in nuclear energy development.

The element always occurs with zirconium in minerals and is recovered commercially as a byproduct in processing zircon to zirconium. The United States and free world resources of hafnium in zircon are very large, but only a small fraction of the zircon consumption is destined to the production of zirconium and hafnium metals.

Four firms with facilities in Oregon, Ohio, West Virginia, New York, and Florida process zircon to hafnium primary products.

The separation of hafnium from zirconium is complicated and expensive. Most hafnium is utilized by the Atomic Energy Commission (AEC) as control rod material in nuclear reactors and in research and development in this field, but this market fluctuates sharply.

The United States is self-sufficient in hafnium and could be self-sufficient in zircon at premium prices.

Major problems confronting hafnium are the lack of commercial uses, high prices, and uncertain markets.

BACKGROUND

Hafnium always occurs with zirconium in minerals, and hafnium is so similar to zirconium chemically that hafnium was not positively identified until 1922.

The Bureau of Mines began developing the Kroll process for producing ductile zirconium-hafnium metal in 1945, and a pilot plant capable of producing 60 pounds of metal a week was started in early 1947. AEC and the Navy Bureau of Ships became interested in the metal, and production capacity increased to 5,000 pounds per month by October 1950 and nearly 25,000 pounds by September 1952 (*6*)[2]. Up to 1950 the hafnium was not removed from the zirconium, as the hafnium content does not detract from many uses of zirconium. However, for nuclear uses, hafnium in zirconium is detrimental, because the presence of hafnium increases the neutron absorption cross section of zirconium greatly and makes it less desirable as a structural material in reactors.

After 2 years' work sponsored by AEC at Oak Ridge, Tenn., a solvent extraction process was developed for the separation of zirconium and hafnium. The Bureau constructed a purification plant utilizing this process and began producing high-purity, low-hafnium (reactor-grade) zirconium in March 1951. Later the Bureau began producing high-purity hafnium sponge in a plant which attained a capacity of 7,000 pounds of hafnium and 300,000 pounds of zirconium by the end of 1953.

Late in 1953, Carborundum Metals, Inc., began producing hafnium-free zirconium and byproduct hafnium oxide, using essentially the process developed by the Bureau. As production at this plant increased, the Bureau plant was shut down July 1, 1955. In March 1956, however, requirements were reappraised and the Bureau plant was reopened, this time to be operated by Wah Chang Corp. under a 2-year contract from AEC to produce 300,000 pounds of reactor-grade zirconium per year. The hafnium oxide from both these operations was delivered to the Bureau of Mines for reduction to sponge metal.

The Bureau ceased hafnium production at the end of 1958. There were AEC contracts for hafnia production with various domestic firms, but these terminated in 1963. Following the loss of this market there was a decline in hafnium production.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Four firms in the United States produce hafnium oxide in connection with zirconium output. They are the Carborundum Metals Co. Division, The Carborundum Co., Parkersburg, W. Va. and Akron, N.Y.; Columbia-National Division, Pittsburgh Plate Glass Co., Pace, Fla.; U.S. Industrial Chemicals Co., Division of National Distillers & Chemical Corp., Ashtabula, Ohio; and Wah Chang Corp., Albany Division, Albany, Oreg. In recent years all of these firms except Columbia National produced hafnium sponge.

[1] Commodity specialist.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

Hafnium crystal bar producers in 1963 were Foote Mineral Co., Exton, Pa.; Wah Chang Corp., Albany, Oreg.; Nuclear Materials & Equipment Corp., Apollo, Pa.; and U.S. Industrial Chemicals Co., Ashtabula, Ohio.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Hafnium (Hf) is a silver-colored metal. Some of its properties are as follows:

Atomic number	72
Atomic weight	178.6
Density—grams per cubic centimeter	13.09
Melting point ° C	2,220
Modulus of elasticity	20×10^{6}
Nuclear properties:	
Thermal neutron absorption cross section barns	115±15
Scattering cross section do	8±2

Hafnium metal as produced by the Kroll process is called hafnium sponge or "Kroll-process" sponge or metal. After refining by the iodide process, the metal is known as crystal bar hafnium, iodide metal, or ductile hafnium. High-purity hafnium derived from electrorefining is also ductile.

Zircon sand concentrate, including the hafnia content, is usually marketed on a basis of 66 percent zirconium oxide (ZrO_2) for domestic material and 65 percent ZrO_2 for imported material. Special high-hafnium zircon such as that from Nigeria usually commands premium prices.

Typical spectrographic analysis of the maximum impurities in hafnium crystal bar and grade 1 hafnium oxide produced by Wah Chang Corp. were reported as follows:

Impurities	Maximum impurities, parts per million	
	Hafnium crystal bar	Grade 1 hafnium oxide
Aluminum	30	<25
Boron	<.5	<.2
Calcium	<50	
Cadmium	<.5	
Cobalt	<10	<5
Chromium	30	<30
Copper	<10	<20
Iron	100	<200
Magnesium	1	<10
Manganese	<10	<10
Molybdenum		<10
Nitrogen	20	
Nickel	10	30
Oxygen	400	
Lead	50	<5
Silicon	30	50
Tin	<10	<5
Titanium	10	30
Vanadium	<20	<20
Tungsten	<50	
Zirconium	10,000–23,000	2,500

TECHNOLOGY

Geology

Hafnium and zirconium always occur together in minerals, but hafnium is always the minor constituent. The earth's crust has been estimated to contain 4.5 parts per million of hafnium compared with 220 parts per million of zirconium. Zirconium is a constituent of many minerals, but only zircon and baddeleyite are sold commercially. Zircon is the lone commercial source for both zirconium and hafnium metal.

Zircon, $ZrSiO_4$, is found as a minor constituent in acid igneous rocks, principally in granites, pegmatites, and granodiorites, in basic igneous rocks such as diabase and basalt, and also in sedimentary rocks such as limestone, sandstone, conglomerate, slate, schist, and gneiss. Zircon is rarely found in hard rock deposits in economically mineable concentrations. However, nature eroded many of these rocks, particularly the granitic rocks, and concentrated the heavy minerals such as ilmenite, rutile, magnetite, and zircon, in sand deposits along rivers, ocean beaches, and in dunes.

Zircon usually contains less than 2 percent hafnia, but there are exceptions. Nigerian zircon is known to contain almost 5 percent hafnia (*2*), and altered zircon may contain as much as 17 percent hafnia.

Baddeleyite, ZrO_2, occurs with zircon in weathered and eroded phonolite in Brazil.

Mining and Concentration

Zircon and baddeleyite are recovered from heavy-mineral beach sands or river gravels as coproducts and byproducts of ilmenite, rutile, monazite, and occasionally gold and cassiterite.

The components of heavy-mineral sands vary in different localities, but are principally magnetite, ilmenite, zircon, garnet, rutile, and monazite with small amounts of other dense and chemically and physically resistant minerals.

Mining of the heavy-mineral sands usually is by conventional dredging methods using bucketline, suction, or dragline dredges. The heavy-mineral rougher concentrator may be on the dredge, or on one or more barges attached to the dredge, or on land. The mineral constituents usually are separated from the rougher heavy-mineral concentrate in a mill on land. Spiral concentrators and electrostatic separators are extensively employed in the recovery and separation of zircon.

Metallurgy (*3*)

To separate hafnium from zirconium requires complicated metallurgical processing. Once separated, further processing of the pure hafnium oxide to metal follows the same methods employed in preparing zirconium.

Production of Crude Tetrachloride

Zircon sand, mixed with graphite or coke, is fused in an electric furnace to produce either the carbides or carbonitrides of zirconium and hafnium. The silica is volatilized as silicon monoxide, while the carbide melt builds up in the bottom of the furnace. When cool, the batch is removed and separated from any unreacted material. The carbide or carbonitride is chlorinated in a vertical-shaft furnace, and volatile chlorides are condensed in a nickel condenser, while silicon and titanium tetrachlorides pass out of the condenser.

Separation of Hafnium From Zirconium

The separation of hafnium from zirconium is costly but necessary to produce the hafnium-free zirconium required for nuclear reactors. Ordinarily zirconium, made without the hafnium separation and containing from 2 to 3 percent hafnium, is suitable for most nonnuclear uses. Separation processes that have been suggested include solvent extraction crystallization, ion exchange, distillation, selective partial reduction, vapor phase dechlorination, fraction precipitation, and caustic leaching, but many of these fall into a group of academic interest (*7*, *8*). Of these, the solvent extraction method has been adopted to the greatest extent. Although many different compounds were tested, among the best were systems using ammonium thiocyanate and methyl isobutyl ketone, or tributyl phosphate and nitric acid.

The crude or commercial grade mixed tetrachloride is dissolved in hydrochloric acid containing ammonium thiocyanate and fed to the top of a vertical glass column. The methyl isobutyl ketone (solvent) enters at the bottom of the column and being lighter than and immiscible with the aqueous solution, it rises upward through the aqueous solution and leaves at the top. As the solvent passes upward it extracts the hafnium thiocyanate preferentially and leaves the column with most of the hafnium and only a small part of the zirconium.

The remaining zirconium is removed by passing the solvent mixture through columns countercurrent to a hydrochloric acid solution, leaving only hafnium in the solvent. The hafnium is recovered from the solvent by passing sulfuric acid solution countercurrent to the solvent, and the resulting hafnium sulfate is converted to hafnium hydroxide by neutralizing with ammonium hydroxide. The hafnium hydroxide is dried and calcined to the oxide. The hafnia content in the hafnium product averages 98.8 percent, the chief impurity being zirconia.

Hafnium Metal Production (*3*, *6*, *8*)

Hafnium oxide is mixed with carbon, sucrose, and a small amount of water, then briquetted, dried, and chlorinated in a vertical-shaft chlorinator.

The hafnium chloride is purified by injecting the vapors into a molten mixture of potassium chloride (KCl) and sodium chloride (NaCl), containing a small quantity of metallic sodium. Impurities, such as aluminum and iron, form complexes with the salt bath and remain in the bath. High-purity hafnium chloride volatilizes from the salt bath and is reacted with a mixture of sodium and magnesium in a reaction crucible. The reaction is exothermic and the temperature is carefully controlled by the rate of addition and by dilution of the gaseous hafnium tetrachloride ($HfCl_4$) with an inert gas. The sodium reacts first, and all of it is reacted before the reaction-zone temperatures attain 800° C. The reduction is completed by the excess of magnesium present.

When the reaction is completed and the furnace has cooled, the crucible with its charge is removed and placed in a distillation furnace where it is heated to about 960° C in a vacuum. The magnesium chloride-sodium chloride binary salt and excess magnesium are melted, volatized, and collected in a condenser attached to the furnace. After cooling, the residual hafnium sponge is removed from the crucible, cleaned in a helium-atmosphere box, and then chopped carefully with a single blade cutter to minus $\frac{3}{8}$-inch.

Refining Hafnium Sponge

Sponge zirconium and titanium, similarly produced, would be ready for melting and fabricating. Hafnium, however, requires additional purification for some uses. Like zirconium and titanium it is hardened and embrittled by oxygen and nitrogen. Kroll-process sponge hafnium contains from 1,000 to 1,500 parts per million oxygen (0.10 to 0.15 percent), and it is necessary to bring this below 500 parts per million to obtain hafnium ductile enough to be rolled, drawn, or extruded readily.

Refining may be accomplished by the iodide process developed by J. H. de Boer (*5*), by electrorefining, or by electron beam (*7*). In the de Boer method hafnium sponge reacts

readily with iodine vapor at about 600° C to form hafnium tetraiodide, which volatilizes. The iodide reversibly dissociates into hafnium and iodine at about 1,600° C. A fine tungsten wire heated electrically provides the heat and energy for decomposition. In a closed system with an inert atmosphere, the iodine can return for more hafnium, with the result that the sponge metal is transferred to the filament where it builds up to a rod from ½ to 1 inch in diameter. Fortunately, hafnium oxide, nitride, and some other impurities transfer at a much slower rate, so the net result is to obtain a very pure and ductile hafnium.

Methods employed by the Metals Co. Division of the Carborundum Co., Akron, N.Y., to process Nigerian high-hafnium zircon to hafnium ingot were published (*1*). The procedures used to process zircon to hafnium ingot are essentially the same as previously described except that hafnium sponge is refined and purified by electrorefining methods, the resultant product being high-purity hafnium flake used to make ductile hafnium shapes.

Melting and Fabrication

Hafnium from the iodide or electrolytic method is melted and fabricated in much the same fashion as zirconium and titanium (*1*, *3*, *6*, *8*). A consumable electrode of the compacted metal is arced against a pool of molten metal in a water-jacketed copper crucible, and the resulting ingot can be fabricated by methods similar to those used for zirconium and titanium.

USES

Zirconium and hafnium metal production have accounted for only a small fraction of the U.S. consumption of zircon as output of this mineral has been used mostly for foundry sands, refractories, ceramics, abrasives, and chemicals.

Hafnium's largest use by far is in nuclear reactors as a control rod material to absorb thermal and epithermal neutrons. It is highly resistant to radiation damage as well as to ordinary chemical corrosion.

A number of applications have been developed for hafnium but very few are in use. Uses developed and suggested are as filaments in electric light bulbs, as electrodes in X-ray tubes, rectifiers, and high-pressure tubes, as a "getter" in vacuum tubes to scavenge traces of oxygen and nitrogen, in photographic flash powders, as a component of detonating caps and ammunition, and in bright coatings for ceramic decoration. A number of hafnium alloy systems have been developed (*4*, *7*).

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Zircon, the commercial source of zirconium and hafnium, usually is recovered as a coproduct but sometimes as a byproduct while dredging heavy-mineral sands for titanium minerals. Zircon output is thus largely dependent upon the demand for titanium minerals.

Hafnium is recovered as a byproduct in processing zircon to zirconium. It is too costly at present to produce hafnium by itself from zircon.

ALTERNATE MATERIALS

Hafnium has preference in nuclear reactors where high cross section and high-temperature corrosion resistance are desirable. It has advantages over substitute materials because it is resistant to water corrosion, is stable under the intense radiation within a reactor, and does not require cladding or other difficult fabrication operations. However, boron, cadmium, samarium, europium, gadolinium, and even gold, silver, and platinum also have high cross sections and have been used for reactor control. Of these, cadmium and boron appear to be most competitive with hafnium. For instance, either hafnium, boron steel, or stainless-steel-clad silver-cadmium-indium alloy control rods have been mentioned as being suitable for pressurized water reactors.

RESERVES

Hafnium is extracted commercially as an impurity from zircon. The zircon resources of the United States and free world were compiled in the 1961 Minerals Yearbook. These figures can be used to estimate roughly the potential hafnium resources by assuming that zircon contains an average of 1 percent hafnium.

The hafnium resources of the United States and free world are shown in tables 1 and 2.

TABLE 1.—*Estimated hafnium resource in zircon of the United States*

State	Zircon, thousand short tons	Hafnium, short tons
California	1,500	15,000
Florida	7,155	71,550
Georgia	345	3,450
Idaho	82	820
Maryland	162	1,620
New Jersey	1,520	15,200
New Mexico, Utah, Wyoming	290	2,900
Oregon	90	900
South Carolina	1,350	13,500
Other States	87	870
Total	12,581	125,810

TABLE 2.—*Estimated hafnium resource in zircon of the free world*

Country	Zircon, thousand short tons	Hafnium, short tons
Australia	2,882	28,820
Brazil	2,552	25,520
Ceylon	1,000	10,000
India	3,360	33,600
South Africa, Republic of	564	5,640
United States	12,581	125,810
Other countries [1]	404	4,040
Total	23,343	233,430

[1] Includes Republic of Ivory Coast, Republic of Korea, Malagasy Republic, Nigeria, and Uruguay.

STATISTICAL INFORMATION, PRODUCTION, AND TRADE

The Bureau of Mines canvasses domestic producers for statistical data on zirconium mineral concentrate, zirconium metal and its alloys and compounds, and hafnium metal and its compounds.

Data on domestic zircon production are withheld to avoid disclosing individual company confidential data. In 1963 the domestic production of hafnia was reported at 65 tons.

The Bureau of the Census collects import and export data on zirconium minerals, and import data on unwrought, waste, scrap, and wrought hafnium. Export data on zirconium and hafnium are not available. Zirconium ore and concentrate are imported duty free. Unwrought hafnium is dutiable at 10.5 percent ad valorem.

STRATEGIC CONSIDERATIONS

The United States is self-sufficient in zirconium and hafnium metals and could be self-sufficient in domestic zircon if required but at increased prices. The AEC has an inventory of hafnium for its use.

GOVERNMENT PROGRAMS

Zirconium mineral concentrate is not being bought by the Government for the national strategic and supplemental stockpiles. Stocks of zircon (1,920 tons) and baddeleyite (16,533 tons) in the strategic stockpile on Dec. 31, 1964, are destined for disposal. Hafnium is not acquired for the national strategic stockpile.

PRICES

Domestic zircon, containing 66 percent ZrO_2, fob Starke, Fla., is quoted at $47 per short ton. Imported zircon containing 65 percent ZrO_2, cif Atlantic ports is quoted at $61 per long ton.

Quoted prices for hafnium sponge and hafnium bar and plate are $75 and $138 per pound, respectively.

TAXES

The domestic depletion allowance is 23 percent, whereas the foreign depletion allowance is 15 percent.

RESEARCH

Hafnium has undergone substantial research and development since 1951 when keen interest focused on its use as control rod material in nuclear reactors.

The production of hafnium was achieved only after a very intensive research program subsidized by the Government through AEC and the Department of Defense. Most of the research was closely associated with the development of zirconium. The Bureau of Mines participated in this program, particularly in developing laboratory processes into workable commercial operations, in developing melting, casting, welding, and other fabrication techniques, and in developing alloys.

Research and development on hafnium at present is mainly on hafnium and zirconium separation and purification, developing alloy systems, and preparation and fabrication of hafnium carbide.

OUTLOOK

The demand for hafnium and its alloys and compounds is expected to increase moderately in the foreseeable future.

Hafnium output will continue to be derived as a byproduct in the recovery of zirconium from zircon even though it might be necessary at times to use high hafnium-bearing zircon as source material for larger yield of hafnium.

The demand for hafnium in nuclear reactors will depend on the demand for new reactors and how well hafnium can maintain its preference over other metals.

Larger consumption of hafnium in established markets and new commercial uses for hafnium through research and development will be vigorously sought.

Hafnium prices will probably fluctuate according to the demand for the metal.

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PROBLEMS

The major problem confronting hafnium is the lack of commercial uses, caused mostly by high prices, uncertain markets, and undeveloped technology.

The largest demand by far for hafnium has been in nuclear energy and in research and development in this field. This demand has varied greatly. Actually, only a few small commercial applications have been developed for the metal. Consequently markets are needed not only to alleviate the fluctuating demand in nuclear energy but also to make greater use of this comparatively new metal.

Currently, hafnium output is controlled by the demand for zirconium as a large portion of the cost of extracting hafnium is borne by zirconium. High hafnium-bearing zircon such as that from Nigeria can be used to increase the yield of hafnium but extraction costs are high and the resources small.

Problems associated with the development of economical hafnium lie in all stages from discovery of new sources through recovery, refinement, disclosure of new physical and chemical properties, and fabrication of the metal and its alloys and compounds.

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HELIUM

By Harold W. Lipper [1]

HELIUM, an element with a rare combination of unique properties and a wide range of vital uses, occurs as a minor constituent of some natural gases. Waste of this limited and irreplaceable resource is curtailed by a long-range helium conservation program carried on by the Bureau of Mines. Large quantities of helium, formerly lost in the burning of helium-bearing natural gas, are recovered and stored for use in the future. Without such a program it is doubtful that enough helium could be recovered from helium-bearing natural gas remaining after 1985 to meet predicted future helium demand (*32*).[2] With the program there is good assurance that adequate supplies of helium will be available beyond the year 2000.

The Bureau owns and operates five helium production plants that supply high-purity helium to meet current demands of the Federal agencies and some commercial customers. Helium to meet future demands is purchased by the Bureau under 22-year contracts in a $47.5 million-a-year helium conservation program from five plants financed, built, and operated by private industry. These plants recover helium that would otherwise be wasted when helium-bearing natural gas is used for fuel and deliver it to a 425-mile pipeline system owned and operated by the Bureau. The purchased helium is stored underground in a partially depleted helium-bearing natural gas formation for later withdrawal and sale. During the life of the present contracts for helium conservation, the five industry plants are expected to deliver 62.5 billion cubic feet of helium. Production from Bureau plants of 15 billion cubic feet would bring the total volume of available helium to 77.5 billion cubic feet. Helium sales are predicted to be 36 billion cubic feet, leaving 41.5 billion cubic feet in underground storage for later use. When the present contracts expire, about 35 billion cubic feet of helium will remain in unproduced, known helium-bearing natural gas sources. The stored helium is likely to be the primary source of supply after about 1985.

Helium has become progressively more important in a wide variety of uses since 1918 when the Bureau and three private firms under U.S. Navy sponsorship pioneered the process for extracting helium from natural gas. Through World War II helium was used almost exclusively as a lifting gas in lighter-than-air ships, and total requirements were met from a few small plants operated by the Bureau. Burgeoning requirements for helium accompanied the technological explosion that followed World War II and taxed severely the capacity of existing plants to supply needs that have grown at 20 percent a year since 1950. Helium use in 1950 was 81 million cubic feet. By 1958 demand rose to 352 million cubic feet, and a plant supplying 300 million cubic feet a year was built by the Bureau at Keyes, Okla., in 1959. Total helium demand for 1964 is expected to be about 700 million cubic feet. Federal agencies will take about 75 percent of the total volume, and the remainder will be delivered to commercial users or distributors who purchase helium from the Bureau for resale. About 6 percent of the total requirement will be met by production from a private plant in Arizona which operates independently of the Government helium program.

More than half the helium used each year is for pressurizing liquid fuels in missiles and space boosters such as Atlas and Saturn. This use and helium-shielded arc welding, leak detection, gas chromatography, helium-cooled nuclear reactors, low-temperature work near absolute zero, synthetic breathing mixtures for undersea exploration, and new uses are expected to require 2 billion cubic feet of helium a year by about 1990.

Fundamental research on helium is carried on by Government agencies, universities, and nonprofit organizations.

[1] Technical assistant, Office of Assistant Director—Helium.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

BACKGROUND

Discovered on the sun in 1868, helium was only known to occur there until 1895, when it was found on earth in a gas extracted from the uranium-bearing mineral cleveite. The occurrence of helium in natural gas, which is the sole source that is of economic interest today, was discovered in 1905. The first effort to use this unique resource was in 1917 when the need for a safe nonflammable gas for airships generated interest in helium. Under sponsorship of the Navy Department, which provided funds and development contracts with private industry, the Bureau began its work with helium in 1918; since 1921 helium has been produced and sold in quantity by the Bureau. Interest in helium for lighter-than-air craft extended after World War I, and the Bureau of Mines built a small helium plant at Fort Worth, Tex., that operated until 1929. A new technology resulted from this pioneering effort, and an economically feasible way was developed for extracting helium from helium-bearing natural gas by a low-temperature gas liquefaction process.

After the loss of the great rigid airships during the 1930's helium consumption declined greatly. However, the Bureau continued helium operations, supplying helium to the Navy for use in nonrigid aircraft, designated blimps, and to the Weather Bureau for use in weather balloons. Minor amounts were sold to research laboratories, hospitals, and industry. During World War II, the Bureau built four new helium extraction plants and enlarged the Amarillo, Tex., plant to provide helium for the many blimps used by the Navy on antisubmarine and other patrols. This military demand for helium soon declined but war-time technology had developed requirements for helium of higher purity than the 98.2-percent product that was adequate for use in lighter-than-air craft. To provide higher purity helium for welding aluminum and other metals, an improved low-temperature helium purification process was designed, developed, and placed in operation during the late 1940's. The new process produced helium having a purity of 99.995 percent and is the basic purification process in use today.

A boom in helium demand began in 1950, almost simultaneously with the availability of high-purity helium. Since then the annual demand for helium has increased about 20 percent a year. Although inactive Bureau plants were returned to production, by 1955 demand exceeded the capacity of the four existing plants. The Exell plant at Masterson, Tex., was enlarged in 1956 to triple its capacity, but the increased production was needed immediately in the Nation's space program. Periodically during the 1950's, helium was in short supply owing to the limited capacity of Bureau plants. Construction of a new plant at Keyes, Okla., in 1959 having a capacity of 300 million cubic feet per year, ended the shortage.

The new plant assured an adequate helium supply for the present, but continuing studies showed that the Nation's future supply of helium depended largely on a long-range conservation program to recover helium that was wasted to the air when helium-bearing natural gas was used for fuel.

Enabling legislation for a long-range helium conservation program Public Law 86–777, amending the Helium Act of 1925 as amended (43 Stat. 1110; 50 U.S.C. 161, 163–166) became effective March 1, 1961. It made helium conservation possible by authorizing long-term (up to 25 years) contracts for the purchase of helium. All of the available contracting authority has been used in 22-year contracts with four companies. The companies financed, designed, and built five plants to extract helium from helium-bearing natural gases that supply fuel markets. The plants deliver helium to the Bureau's pipeline system where it is transported to the Cliffside gasfield near Amarillo, Tex. Helium acquired for conservation is stored underground in the gasfield for later withdrawal and purification to augment the supply available from remaining helium-bearing gas supplies. Additional information concerning the helium conservation contracts is shown in table 1.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Until late 1961 the only helium extraction plants in the free world were the five plants owned and operated by the Bureau of Mines. Completion of the Kerr-McGee Oil Industries, Inc., plant at Navajo, Ariz., in December 1961 marked the first private industry production, independent of the Government's helium program, since the 1930's when small private plants were operated for a time at Dexter, Kans., and Thatcher, Colo. The Bureau plants, the Kerr-McGee plant, and a small plant in Canada produce and market high purity helium. The five plants built by industry in the long-range helium conservation program produce a product called crude helium, which is a mixture of helium and nitrogen.

TABLE 1.—*Contracts for helium conservation*[1]

Company (parent companies in parentheses)	Plant location	Initial unit price (1,000 cubic feet)	Maximum annual obligation (millions)	Estimated helium volume (million cubic feet)	
				Annual average	Life of contract
Northern Helex Co. (Northern Natural Gas Co.).	Bushton, Kans	$11.24	$9.5	675	13,500
Cities Service Helex, Inc. (Cities Service Co.).	Ulysses, Kans	11.78	9.1	610	12,200
National Helium Corp. (Panhandle Eastern Pipe Line Co. and National Distillers & Chemical Corp.).	Liberal, Kans	11.78	15.2	1,053	21,060
Phillips Petroleum Co	Dumas, Tex., and Hansford County, Tex. (2 plants).	10.30	13.7	788	15,766
Weighted average		11.29			
Total			47.5	3,126	62,526

[1] All contracts were let during 1961.

At the Bureau's Exell, Tex., Keyes, Okla., and Otis, Kans., plants, supplies of helium-bearing natural gas for processing are obtained through contracts with private companies that own and control the respective gas supplies. Helium-bearing natural gas from company pipelines is diverted to the plants. After the helium is extracted, the remaining natural gas is returned for transmission to fuel markets. Shrinkage of the helium-bearing natural gas stream through Bureau plants averages about 8 percent of the inlet volume. Such shrinkage comprises the helium and a small amount of nitrogen that is removed with the helium plus the natural gas used as fuel at the plants.

Helium-bearing gas for the Amarillo, Tex., plant comes from the nearby Cliffside gasfield in which the Government has owned gas rights since 1929. After removal of helium, the remaining natural gas is sold by the Government under a life-of-the-field contract to a gas-producing company for disposal as fuel. At the Bureau's Navajo helium plant near Shiprock, N. Mex., helium-bearing natural gas is obtained under gas purchase contracts from nearby privately developed wells. The gas is nonmerchantable as fuel because of its low heating value.

At Navajo, Ariz., the Kerr-McGee plant extracts helium from a company controlled source, the Pinta Dome field. Here the gas is essentially a mixture of helium and nitrogen (*27*). A similar situation exists in connection with the Canadian Helium Limited plant in Saskatchewan, Canada, near Swift Current (*25*). Table 2 gives capacity and other data for all known helium extraction plants in the free world.

DEFINITION OF TERMS, GRADES, SPECIFICATIONS, AND PROPERTIES

All helium produced at Bureau plants is 99.995 percent pure and is designated grade A. Other gases (mainly neon, nitrogen, and hydrogen) total not more than 50 parts per million by volume (*16*). The Bureau sells helium in no other grade. Grade A helium is measured as a gas in cubic feet at a base pressure of 14.7 pounds per square inch absolute at 70° F. The Kerr-McGee plant furnishes helium that is comparable to the Bureau's Grade A helium.

Helium purchased by the Bureau for conservation is a mixture of helium and nitrogen, but small amounts of hydrogen and hydrocarbons may be present. The mixture is measured at a base pressure of 14.65 pounds per square inch absolute at 60° F. Payment is for the helium contained in the mixture delivered to the Bureau's pipeline.

Helium is a monatomic, chemically inert gas. Next to hydrogen it is the lightest of all gases. At 14.7 pounds per square inch absolute and at 70° F, 1,000 cubic feet of helium weighs 10.34 pounds. A like volume of air would weigh more than 76 pounds. Helium liquefies at −452.13° F, just 7.69° F above absolute zero. Liquid helium is generally sold by the liter. A liter of liquid helium is equivalent to 26.63 cubic feet of gas. Helium remains liquid down to essentially absolute zero and is the only gas known to behave in this manner. It solidifies or freezes only under pressure. Publications listed in the references section (*2–3, 10, 26*) present additional information on the properties and characteristics of helium.

TABLE 2.—*Data on helium plants*

Plant	Ownership	Initial operation	Approximate average helium content of gas stream (mole-percent)	Approximate annual capacity (million cubic feet)	Helium content of product (mole-percent)
High-purity helium plants:					
Amarillo, Tex.	Bureau of Mines	April 1929	1.8	60	99.995
Exell, Tex.	do	March 1943	.9	280	99.995
Otis, Kans.	do	October 1943	1.4	50	99.995
Navajo (Shiprock), N. Mex.	do	March 1944	5.7	80	99.995
Keyes, Okla.	do	August 1959	2.0	300	99.995
Navajo, Ariz.	Kerr-McGee Oil Industries, Inc.	December 1961	8.2	65	99.995
Swift Current, Saskatchewan, Canada.	Canadian Helium Limited.	December 1963	1.9	12	99.995
Total				847	
Conservation plants:					
Bushton, Kans.	Northern Helex, Inc.	December 1962	.46	675	60.0
Hansford County, Tex.	Phillips Petroleum Co.	do	.78	[1]788	50.0
Dumas, Tex.	do	April 1963	.65		50.0
Ulysses, Kans.	Cities Service Helex, Inc.	June 1963	.43	610	60.0
Liberal, Kans.	National Helium Corp.	July 1963	.40	1,053	60.0
Total				3,126	
Grand total				3,973	

[1] Combined capacity—2 plants.

TECHNOLOGY

A survey to determine the Nation's helium resources has been carried on in all natural gas producing areas of the United States since inception of the Government's helium program in 1917. Sampling and analysis techniques have been described in detail (*1, 4, 22–24*).

Some large natural gasfields contain no helium, or helium is present only in trace amounts (less than 0.05 percent). Gas from the Hugoton and Texas Panhandle gasfields normally contains 0.3 to 1.0 percent helium. Some relatively small, isolated fields, such as the Table Mesa and Hogback fields of New Mexico, contain gas having about 5.5 percent helium. Gas from the Pinta Dome field contains 8.2 percent helium.

Helium is extracted from helium-bearing natural gas by a low-temperature gas liquefaction process (*12*). At Bureau plants the helium-bearing natural gas stream is cooled to a temperature that is below the liquefaction point of the hydrocarbon components but is above the liquefaction point of helium. A separation is then made of the gas, which is mostly helium, and the liquid, which is mostly hydrocarbons. The product of this separation is called crude helium, which is a mixture of about 70 percent helium and 30 percent nitrogen. The crude helium is compressed, cooled until most of the nitrogen is removed, and passed through activated charcoal at the temperature of liquid nitrogen (−320° F), for final purification. The resulting 99.995-percent pure helium is then put into shipping containers.

Although the basic low-temperature helium extraction process in use today was developed by the Bureau of Mines, the technology for helium extraction took great strides forward when the five new helium conservation plants were built. Daily helium-bearing natural gas processing capacity of the plants for helium conservation is 7 to 11 times greater than that of the largest Bureau plant. This feature required the design and construction of some of the largest heat exchangers ever built for low-temperature processing applications. Because of the low-helium content of the large natural gas volumes processed, there were stringent requirements for essentially complete helium recovery.

The Kerr-McGee plant in Arizona also produces liquid helium. During the past 5 years

the technology of helium liquefaction has more than kept pace with increased requirements. Air Reduction Co., Richmond, Calif., Gardner Cryogenics, Hightstown, N.J., and Linde, Amarillo, Tex., also operate large helium liquefiers. The estimated total capacity of the major commercial helium liquefaction plants is 525 liters an hour. Plans have been announced for a 500-liter-an-hour plant to be completed in Kansas during 1965 (*8*). In addition, many laboratories and development centers have their own small liquefiers. Capacities are a few liters of liquid helium an hour, but from 200 to 300 such liquefiers are distributed throughout the free world.

There are two naturally occurring stable isotopic forms of helium; helium 3 with an atomic mass of 3.0169 and helium 4 with an atomic mass of 4.0038. Helium produced from natural gas is predominately the heavier variety; only 0.00013 mole-percent helium 3 is present. Helium 3 has properties unlike those of helium 4 which make it useful for many scientific investigations at temperatures within a few tenths of a degree of absolute zero. The chief source of helium 3 is Mound Laboratory, Miamisburg, Ohio, which is operated for the Atomic Energy Commission by Monsanto Research Corp. Helium 3 from the laboratory is a product of nuclear reactor technology (*13*).

USES

The Bureau of Mines canvassed its helium customers to obtain information on their use of helium during calendar year 1962. In the period covered by the survey, the Bureau shipped 600 million cubic feet of helium. About 78 percent, or 468 million cubic feet, went directly to Federal agencies, and 22 percent, or 132 million cubic feet, went to non-Federal customers. In addition, the Kerr-McGee plant reportedly sold about 30 million cubic feet to non-Federal customers. Thus, the total helium shipments and assumed use during 1962 was 630 million cubic feet. Total helium consumption in 1962 is summarized in table 3 and compared with consumption in 1955 by non-Federal customers. At that time, the Bureau was the sole quantity producer of helium in the United States.

TABLE 3.—*Utilization of helium in 1962*

Use	Overall use	Federal agency use	Private company use	Private company use on Government contracts	Federal agency use and use on Government contracts	Non-Government use	Private company use in 1955 [1]
Pressurizing, volume-percent	45.0	60.5	0.5	1.0	52.5	--------	[2]
Welding, do	15.0	7.0	38.0	50.0	12.5	30.0	64.5
Controlled atmosphere, do	12.5	11.0	17.0	6.0	11.0	21.5	[3] 16.4
Research, do	11.0	8.0	19.5	25.0	10.5	14.0	5.1
Lifting gas, do	5.5	7.0	1.0	1.5	6.0	2.5	1.2
Purging, do	3.0	3.0	3.0	2.5	2.5	6.0	[2]
Leak detection, do	2.5	.5	8.0	7.0	1.5	8.5	8.0
Cryogenics, do	1.5	1.5	1.5	3.0	1.5	1.5	[2]
Chromatography, do	1.5	--------	6.0	1.0	----------	10.0	[2]
Heat transfer, do	1.0	1.0	1.0	.5	1.0	--------	[2]
Other [4], do	1.5	.5	4.5	2.5	1.0	6.0	4.8
Percent of total volume	100	74	26	11	85	15	27
Volume, million cubic feet	630	468	162	71	539	91	[5] 64

[1] Compare with private company use in 1962.
[2] No information obtained in 1955.
[3] Includes percentages of use for titanium production and fabrication, transistors, and zirconium production in 1955.
[4] Includes uses for synthetic breathing mixtures, medical, tracer, and miscellaneous purposes.
[5] Total helium use in 1955 was 236 million cubic feet.

Helium is used for pressurizing purposes in liquid-fueled missiles and space vehicles. For boosters, such as Atlas and Titan I, helium provides pressure to push fuel into the pumps that supply the rocket engines. In the Atlas, helium serves an important secondary purpose by filling the thin-skinned fuel tanks, as the fuel is consumed, to provide the rigidity necessary to prevent collapse and failure of the tanks in flight. Helium is also used as a pressurizing medium for testing many of the delicate and intricate piping assemblies and components on which successful launches depend. Development of the large Saturn-class liquid-fueled rocket engines will require increasing volumes of helium for test and operational purposes.

Shielded-arc welding continues to require large volumes of helium and is the largest single

industrial use. In addition to building ships, aircraft, spacecraft, and rocket structures, helium is used in the welding process for items such as food-handling equipment, photographic developing equipment, diesel engine parts, hardware, architectural shapes, and electrical devices, and in the manufacture of many other products made from stainless steel, aluminum, copper, titanium, and zirconium. Much of the helium used for welding is a mixture of 75 percent helium with 25 percent argon.

Helium serves a variety of purposes as a controlled atmosphere. It is used in growing germanium and silicon crystals for transistors, in processing fuels for nuclear energy purposes, and for cooling vacuum furnaces.

In research, helium is used for all the purposes listed in table 3. Other uses include aerodynamic research using helium in wind tunnels and shock tubes, study of adsorption techniques, development of improved seals and valves for positive shutoff, pharmaceutical and biological research, particle physics investigations, development of improved light sources, radiation detection devices, plasma arc studies, mass transfer studies, tensile and impact tests of materials, solid state physics, and development of new techniques for X-ray analysis. Research involving the behavior of materials at temperatures near absolute zero, such as the development of superconducting magnets, requires the use of significant amounts of liquid helium. Some metals and alloys become superconductors at liquid helium temperatures; they offer no resistance to the flow of electricity, and a current once started will flow undiminished as long as the current-carrying material is kept at liquid helium temperature. Superconducting magnets have been built that produce intense magnetic fields at a fraction of the weight and power requirements of conventional magnet systems. Other uses of superconductors may materialize such as in lightweight, efficient power generators and for more efficient long-distance transmission of electric power.

About 35 million cubic feet of helium was used during 1962 as lifting gas. Only two Navy blimps were in service then. These were decommissioned in the fall of the year, and the helium recovered for reuse in other activities. Over half of the 35 million cubic feet was used in balloons to obtain weather information. Most of the remainder was used in balloons that carried special instruments to about 100,000 feet to measure particles entering the earth's atmosphere from space and to make telescopic observations unhindered by the obscuring effects of the earth's atmosphere. The volume used in toy balloons was estimated to be slightly over 1 million cubic feet. Some helium was used in lighter-than-air craft devoted to advertising. The volume of helium used as a lifting gas during 1962 is more than twice the peak helium consumption of 15 million cubic feet for rigid airships during 1930–33.

Use is made of the ease and rapidity with which helium passes through minute openings in detecting leaks or more often in verifying the absence of leaks in a variety of operations and products. Sensitive helium detection devices reportedly can identify helium leaks so small that 3,000 years would be required for a liter of helium to pass through the opening. The method is used to assure freedom from leaks in component parts and piping systems of nuclear reactors, metallic bellows assemblies, electron tubes, hermetically sealed electrical devices, and other items where safe operation or satisfactory service life depend on leakproof characteristics. The relatively large volume of helium used in leak detection exclusively for commercial purposes was primarily to assure a high-quality product.

One of the newer uses for helium is as a carrier gas in chromatography. The principles of chemical analysis by chromatographic means have been known for some time but requirements arising in recent years for higher purity products, more rapid analysis, and greater product yields have stimulated the use of chromatographs in the refining, petrochemical, food processing, drug, and chemical industries. A single chromatograph requires only a small volume of helium annually, but the cumulative effect of a large number of instruments is apparent in the more than 9 million cubic feet used for this purpose.

Another recent use of helium is for heat transfer purposes, primarily in gas-cooled nuclear reactors for power generation. One such reactor near Philadelphia, Pa., is nearing operational status, and others are in the planning stage. Helium does not become radioactive, has good characteristics for removing heat from the nuclear fuel, and reportedly permits better efficiencies by making it possible to operate a reactor at higher temperatures than would be possible with other coolants.

Small, but important, volumes of helium mixed with oxygen continue to be used in the treatment of asthma and other respiratory ailments. Helium is also used as a diluent for anesthetics and as a tracer. Helium-oxygen breathing mixtures have been used by Navy divers for many years because helium is much less soluble in the blood than the nitrogen in normal air mixtures. Recent experiments with high-helium, low-oxygen breathing mixtures hold promise for showing the way for man to live in the sea almost as readily as he now lives on land (*11*, *15*, *19*). Further development of techniques to permit man to work in the ocean

depths would allow exploration and possible exploitation of the vast resources known to lie on or beneath the sea floor.

ALTERNATE MATERIALS

Although few, if any gases have the combination of unique properties that characterize helium, there are applications where substitution is possible. Nitrogen, for instance, may be used for pressurizing liquid oxygen, but at some sacrifice in oxygen quality because of the high solubility of nitrogen in liquid oxygen. Helium, being only slightly soluble in liquid oxygen and other liquids, has little, if any, degrading effect upon them. Consequently, helium is preferred for pressurizing and blanketing operations where reliability and freedom from contamination are of paramount importance.

In shielded-arc welding and other metallurgical processes, helium, argon, or mixtures of the two gases are used to provide an inert gas shield to prevent formation of impurities in the molten metal. For certain welding jobs, the use of helium alone is preferred because welding can be done more rapidly and with less porosity than with other gases. In some instances the higher thermal conductivity of helium offers advantages not possible with argon.

Either hydrogen or helium may be used for inflating balloons and lighter-than-air craft. Hydrogen, being lighter than helium, will provide about 7 percent more "lift" in air but is seldom used in large quantities because of its flammability hazard. This hazard does not exist with helium. Hydrogen may be used instead of helium as the carrier gas in chromatographic analysis equipment. However, in addition to being flammable, hydrogen will combine chemically with the product being analyzed or controlled. Other gases, such as argon, do not provide the sensitivity that is sometimes desired. Helium is preferred as a carrier gas generally because of its inertness and high thermal conductivity.

Carbon dioxide and nitrogen can each be used in gas-cooled nuclear reactors, but helium is preferable. Helium does not corrode the piping, does a better job of transferring heat from the reactor, and does not become radioactive.

In all of the foregoing applications, helium is used primarily because it has some inherent advantage over other materials that might be used. No substitute materials are available in the field of cryogenics, where there is need for temperatures near absolute zero (−459.72° F.). Helium becomes liquid at −452.13° F., a temperature well below the point where all other gases solidify. In fact helium is the only material known that remains liquid at temperatures within a few tenths of a degree of absolute zero.

RESERVES

The presently known or measured helium resource of the United States in helium-bearing natural gas containing three-tenths (0.3) volume-percent or more helium was estimated to be 196 billion cubic feet as of January 1, 1961. Of this volume, probably no more than 154 billion cubic feet can be recovered for use. About 94 percent of the helium resource is contained in the following five helium-bearing gasfields: (1) the Hugoton field of Kansas, Oklahoma, and Texas; (2) the Panhandle field of Texas; (3) the Keyes field of Oklahoma; (4) the Greenwood field of Kansas and Colorado; and (5) the Cliffside field of Texas. The remaining 6 percent is in smaller scattered and isolated fields.

All of the helium-bearing natural gas reserves were discovered by private companies, and most of the reserves are dedicated to supply fuel markets. Consequently, where helium-bearing natural gas is produced without regard for its helium content, the helium, having no value as fuel, is lost.

Helium-bearing natural gas sources available to the five Bureau plants and the five industry plants that recover and sell helium to the Bureau in the helium conservation program represent about 70 percent of the total known helium resource. An additional 20 percent of the total helium resource that could be recovered at costs comparable to present costs is being wasted. The remaining 10 percent is considered a marginal resource, although special circumstances might make recovery of helium economically feasible in specific instances. The effect of such recovery on total helium resource is likely to be small.

Some of the oilfields and gasfields discovered in the past few years in eastern Utah and western Colorado contain helium. However, the helium reserves in these fields are limited, comprising only about 3 percent of the national total. Natural gas production from these fields is also limited, and the resulting wastage of helium amounts to a still smaller percentage of the total annual waste. The prospects for finding new sources of helium comparable with those now known appear poor. The last discovery of a significantly large reserve of helium-bearing gas was in 1943 when the Keyes field in Oklahoma was found.

With the possible exception of the Soviet Union, no country has helium reserves comparable with those in the United States. Canada is the only country in the free world known to produce helium, but the reserves discovered

so far are small compared with those in the United States. Helium-bearing natural gases offer the only presently known economical sources for producing helium. However, there are other occurrences of interest, including gases from mineral springs, fumaroles, and volcanoes; rocks; minerals; certain sands; and meteorites. Helium can also be formed by nuclear bombardment and fusion. It is present in the air in the ratio of about 1 part helium to 200,000 parts air.

CONSERVATION PRACTICES

Conservation in the sense of full and wise use of our Nation's helium resource is the purpose of the Bureau's helium program. Since completion of the Bureau's Keyes, Okla., helium plant in 1959, helium has been in plentiful supply; future supplies are expected to be adequate to meet a threefold increase in annual needs. However, present estimates of continued increased demand for helium will require the purification and sale in the near future of helium obtained from private industry in the long-range helium conservation program.

Although present supplies of helium-bearing natural gas can supply many times the volume of helium presently used each year, these gas supplies, and consequently the Nation's reserves of helium, are limited. Instead of permitting helium resources to be wasted when helium-bearing natural gas is used as fuel, the previously mentioned $47.5 million-a-year conservation program authorized by Congress is in effect to assure that helium is available for use in the future. During the life of the contracts for helium conservation, the Bureau expects to purchase 62.5 billion cubic feet of helium as shown in table 1. Production from Bureau plants is expected to be about 15 billion cubic feet. Thus, the total volume available between 1960 and 1983 is 77.5 billion cubic feet. Demand during the period is expected to be 36 billion cubic feet. The remaining 41.5 billion cubic feet will be stored underground for later use. Use trends for helium indicate growth in annual demand from the present level of 700 million cubic feet to 2,000 million cubic feet by about 1985. Thus, helium placed in underground storage now will be available to augment production from available helium-bearing natural gases when this source can no longer meet annual demand. The present program for helium conservation is expected to meet foreseeable needs beyond the year 2000.

Although extraction of helium from helium-bearing natural gas in advance of burning the gas as fuel is the primary conservation practice in effect today, some users find it economical to salvage helium and repurify it for reuse. Wind tunnel installations using helium for testing models at supersonic velocities were among the first to install equipment for reclaiming helium. Generally, the helium mixed with air or other contaminants is captured in a large bag and then is passed through a low-temperature adsorption process for purification and reuse. Some closed-cycle helium refrigeration systems employ repurification to maintain the high quality of helium in the system. At present the total volume of reclaimed helium is small.

SOURCES OF STATISTICAL INFORMATION

The Bureau's records of its operations are the source of information on occurrence of helium and on the volume of helium produced, shipped, and stored. Estimates of helium end use are obtained through the cooperation of customers. General information on helium produced independently of the Government's program is made available to the Bureau through the cooperation of the private producer.

PRODUCTION AND CONSUMPTION

Helium production from the five Bureau plants in 1963 totaled 774.2 million cubic feet, an increase of 7 percent over the record set in 1961. About 35 million cubic feet of helium was produced by the Kerr-McGee Oil Industries, Inc., plant. Production from Bureau plants since the beginning of operations in 1921 through 1963 was 5.9 billion cubic feet; almost half of this was produced since 1959. Table 4 shows production from 1921 to 1963.

TABLE 4.—*Helium production in the United States*

[Million cubic feet]

Year	Quantity	Year	Quantity
1921–28	[1] 5.8	1960	642.0
1929–42	[1] 11.8	1961	727.1
1943–49	[1] 83.5	1962	683.1
1950–54	[1] 138.0	1963	2,194.0
1955–59	[1] 313.4	Total 1921–63	[2] 7,299.3

[1] Annual average.
[2] Does not include helium produced at the privately owned Kerr-McGee plant but includes helium purchased for conservation.

Conservation helium purchased by the Bureau in 1963 is as follows:

Plant	*Helium delivered (million cubic feet)*
Northern Helex Co	208
Cities Service Helex, Inc	75
National Helium Corp	457
Phillips Petroleum Co., Dumas, Tex	198
Phillips Petroleum Co., Hansford County, Tex	482
Total	1,420

Helium placed in conservation storage from 1960 to 1963 is as follows:

Year	Million cubic feet
1960	273
1961	447
1962	524.6
1963	2,110

Table 5 shows helium consumption in the United States from 1950 to 1963.

TABLE 5.—*Helium consumption in the United States*

[Million cubic feet]

Year	Quantity	Year	Quantity
1950	81	1957	310
1951	109	1958	352
1952	145	1959	375
1953	158	1960	475
1954	190	1961	551
1955	236	1962	630
1956	267	1963	662

The total volume of helium extracted from natural gas during 1963 in the Government's helium program totaled 2,194 million cubic feet. Production from Bureau plants was in excess of demand, and no helium was withdrawn from the conservation supply. The excess production from Bureau plants, 165 million cubic feet, was stored underground. In previous years, the Bureau has stored in the Cliffside field small quantities of helium produced at its plants in excess of market requirements.

Helium shipments from Bureau plants totaled 627.3 million cubic feet. Federal agencies received 473.7 million cubic feet, and 153.6 million cubic feet was sold to non-Federal customers. Table 6 shows Bureau helium shipments. In delivering helium to customers, Bureau plants filled and shipped 1,820 tank cars, 1,212 trailers, and 262,088 standard gas cylinders.

Helium exported by commercial distributors and civilian agencies of the Federal Government in 1962 is shown in table 7. The figures do not include helium used abroad by the defense agencies. Most helium exported to Canada, France, and the United Kingdom was used in atomic energy programs and for experiments at low temperatures. That exported to Japan was used in low-temperature research and for gas chromatography. Helium is exported under licenses issued by the Office of Munitions Control, U.S. Department of State.

STRATEGIC CONSIDERATIONS

The United States is self-sufficient in helium, although total resources are limited and irreplaceable. Helium purification equipment installed at Bureau plants to handle production during seasonal periods of peak supplies of helium-bearing natural gas can be used to augment production by purifying crude helium purchased for conservation. Thus, Bureau plants could, on demand, increase total output of high-purity helium to nearly 850 million cubic feet a year.

Helium placed in underground storage in the long-range conservation program will meet the year-to-year growing demand for helium and assures that large increases in demand could be accommodated on short notice.

TABLE 6.—*Shipments of helium from Bureau of Mines helium plants in 1963*

	Million cubic feet	Percent
Federal agencies:[1]		
Department of Defense	337.3	53.8
Atomic Energy Commission	75.5	12.0
National Aeronautics and Space Administration	52.6	8.4
Weather Bureau	7.8	1.2
Other	.5	.1
Total	473.7	75.5
Non-Federal consumers	153.6	24.5
Total shipments	627.3	100.0

[1] Actual use by the Federal agencies is not reflected by the deliveries shown. The Weather Bureau obtains about as much helium from the Navy as it receives from the Bureau of Mines. The Navy also furnishes helium to the National Aeronautics and Space Administration and Air Force installations.

TABLE 7.—*U.S. exports of helium in 1962*

Country	Thousand cubic feet	Country	Thousand cubic feet
Belgium	108.0	Japan	1,040.0
Canada	3,010.0	Mexico	360.0
Denmark	4.0	Netherlands	14.0
Finland	4.0	Nicaragua	1.0
France	1,327.0	Norway	4.0
Germany, West	839.0	Portugal	.5
Greece	1.0	Sweden	25.0
Guatemala	1.0	Switzerland	289.0
India	1.0	Taiwan	12.0
Israel	77.0	United Kingdom	1,868.0
Italy	76.0		
Jamaica	.5	Total	9,062.0

PRICES

The revised Helium Act (Public Law 86–777) directs agencies of the Federal Government to purchase all major helium requirements from the Secretary of the Interior and provides that helium shall be sold at prices adequate to cover all costs of carrying out provisions of the act, including repayment to the Treasury of the United States, with interest, of all funds that may be borrowed to sustain the program and all capital and retained earnings as of the effective date of the act.

Until November 18, 1961, sales were at prices established in 1954 of $15.50 and $19 a 1,000 cubic feet (f.o.b. plant) for Federal and non-Federal purchasers, respectively. A price to

cover all costs of carrying out the provisions of the Helium Act and to make the prescribed repayments was calculated to be $35 a 1,000 cubic feet. On November 18, 1961, the increased price went into effect and is applicable to all users. Revised regulations, a schedule of charges, and other information on the sale of helium and rental of containers by the Bureau are included in the Code of Federal Regulations (30 CFR 1).

TRANSPORTATION

Over 80 percent of the helium shipped from Bureau plants is delivered to customers in railway tank cars of special design. The rest is delivered in truck semitrailers and standard compressed gas cylinders. Shipments in cylinders by the Bureau are made exclusively from the Amarillo plant. Other Bureau plants ship helium in tank cars and semitrailers. The Navajo plant is about 90 miles from a standard gage railroad. It is connected to a tank car loading facility at Gallup, N. Mex., by a 2-inch high-pressure helium pipeline.

A typical tank car is constructed of 30 steel cylinders, 18 inches in outside diameter and 33 feet long, mounted in a specially constructed frame. Cylinders on the cars are designated ICC 107A (*9*). Permissible filling pressures of individual tank car cylinders range from 1,745 to 4,000 pounds per square inch gage. Cars suitable for filling at the higher pressures will contain about 300,000 cubic feet of helium measured at base conditions of 14.7 pounds per square inch gage and 70° F. (*14*). An empty tank car weighs about 220,000 pounds. The helium in a full car weighs between 2,000 and 3,000 pounds. Freight charges are based on an arbitrarily prescribed minimum carload weight of 40,000 pounds.

Except for a few tank cars owned by other Government agencies, the Bureau's 236 tank cars are the only ones of their kind in use for rail shipment of helium as a compressed gas.

Truck semitrailers are constructed in a manner similar to railway tank cars, but they are smaller and lighter in weight. Tubes for trailers must also meet ICC specifications. The Bureau owns five semitrailers, each having capacity to deliver about 100,000 cubic feet of helium, and two newer trailers that will deliver about 140,000 cubic feet each. The trailers are used primarily in the service of customers whose requirements do not lend themselves to delivery in tank cars. Commercial distributors who purchase helium from the Bureau for resale, a Federal agency, and a contract carrier also own several large-capacity trailers. Smaller trailers, which will deliver from 29,000 to 50,000 cubic feet of helium are owned by the Atomic Energy Commission, the Army, the Navy, and commercial distributors.

Standard helium cylinders hold 213 to 265 cubic feet when filled to 2,000 to 2,400 pounds per square inch gage. The cylinders meet ICC–3A or ICC–3AA specifications. They are shipped in railway boxcars and motortrucks. The Bureau has about 100,000 cylinders for lease to customers, although many users supply their own. An empty cylinder weighs 122 to 137 pounds, and a full cylinder weighs about 2½ pounds more.

The costs of transporting helium as a compressed gas make up a significant part of the delivered price because relatively small amounts of helium can be delivered in proportion to the weight of the container. Recent reductions of 31 percent in the rates for shipment of helium in railway tank cars to the Federal agencies will, at present levels of helium use, save the Federal agencies about $700,000 a year.

A private company has announced plans to transport as liquid the entire production of a proposed private helium liquefaction plant. The plan includes 10,000-gallon tank trailers suitable for transporting liquid helium cross country for subsequent distribution as gas and as liquid (*8*). Ten thousand gallons of liquid helium is equivalent to about 1 million cubic feet of gaseous helium.

The high-purity helium obtained by the purification process or from evaporated liquid may be reduced by contamination from piping and from the containers into which it is eventually put for use. Consequently, where high-purity helium is essential, producers and users alike keep helium handling lines and containers scrupulously clean.

RESEARCH

Until 1961 the Bureau carried on a small research program that was aimed primarily at solving helium production problems and improving processes for the recovery and purification of helium. Research emphasis changed in 1961 and is now directed toward learning more about the properties of helium for the purpose of eventually increasing its utility. Thermodynamic and other data for helium are being reviewed systematically with the objective of identifying "best" values and closing gaps in data by experiments as warranted. Work is underway on projects that include development of a method for measuring the heat capacity of helium and its mixtures with other gases, measurement of the absolute viscosity of helium, diffusion coefficients, the solubility of helium in liquefied gases, and investigation of metastable energy levels in liquid helium. Publication of

research completed at the center includes values for phase equilibria of helium gas mixtures (*5–6, 28–30*) information on the compressibility of gases (*7, 20–21*); continuous analysis of helium in natural gas (*17*); and an apparatus for detecting helium leaks (*18*). A bibliography published in 1952 lists more than 2,600 technical and scientific articles relating to helium (*33*).

Fundamental research on helium is carried on by educational institutions; nonprofit organizations; and Government agencies, such as the National Bureau of Standards, U.S. Atomic Energy Commission, and U.S. Department of Defense. The unusual properties of helium at temperatures near absolute zero continue to be the subject of intensive research despite decades of effort. The results of research on helium are reported regularly, and listings are published in "Chemical Abstracts," "Nuclear Science Abstracts," "Physics Abstracts," Technical Abstract Bulletins," and other abstract services.

OUTLOOK

Although helium is a limited and irreplaceable resource, the long-range helium conservation program carried on by the Department of the Interior assures our Nation a continuing adequate supply for the immediate future and further, has the potential for meeting large-scale requirements for helium well into the 21st century. Fortunately, because of today's far-sighted program, the emphasis on helium can be its wise and effective use rather than measures to lock up the supply for limited use (*31*).

Helium consumption in the United States has increased since 1950 at an average of 20 percent a year. During 1960–64, the rate was 13.5 percent; 475 million cubic feet was used in 1960 compared with about 700 million cubic feet in 1964. Most of the increase was due to the use of helium in the development, testing, and launching of liquid-fueled boosters, such as Atlas and those of the Saturn series. Growth projections made by the Bureau in 1959 indicate that by the year 2000 annual helium consumption will approach 2 billion cubic feet. Experience during the past 5 years agrees well with the 1959 projection. The historic pattern of new applications supplanting old ones is expected to continue, with the effect of broadening the scope of helium uses for scientific, industrial, and defense purposes. Helium to meet these larger demands is expected to be available from the helium-bearing natural gas available for processing at existing extraction plants until about 1985. When helium from this source is no longer adequate to meet annual demand, withdrawal of helium stored underground will begin. As supplies of helium-bearing natural gas decline, reliance must be placed on helium in underground storage. According to present expectations, foreseeable requirements for helium should be met well past the year 2000.

Breakthroughs in science to apply superconductors to long-distance transmission of power and other uses of the low temperatures that can be produced only with helium would require large quantities. Further development of the technology of maintaining artificial atmospheres containing helium to permit man to colonize the sea and develop its riches could require tremendous volumes. These and other uses for helium are near reality today. Tomorrow's new and unforeseen uses could place severe burdens on helium supplies sometime in the 21st century. Then, small isolated sources of helium-bearing gases should become more important and will probably be developed. As these are exhausted, it may become necessary to turn to the atmosphere or to controlled nuclear reactions for helium. Discovery of large new natural sources of helium could change this picture, but based on past experience, the prospects are not good for discovering new sources comparable with those now known in developed gasfields.

As further progress is made in reducing the useless waste of helium into the atmosphere from the burning of helium-bearing gases, and as the economics of doing so are improved, more attention must be given to reclaiming helium for reuse. When these measures are inadequate to assure a continuing supply, some form of end-use controls will surely be required.

PROBLEMS

The overall long-range problem concerning helium continues to be one of rapidly growing helium demand in the face of diminishing helium resources.

More immediate problems concern the cost of transporting helium from the producer to the consumer. Most other gases are or can be produced near the place of use. Helium, on the other hand, occurs in a limited area far from where it is used. Containers for transporting helium as a compressed gas are heavy and hold only 1 or 2 cubic feet of helium for each pound of container. In the past, the high shipping costs have represented a disproportionate part

of the ultimate cost of helium to the consumer. Reduction in freight rates for shipping compressed helium have reduced the delivered cost of helium to the Federal agencies. Nevertheless, as the technology for doing so is improved, the shipment of helium as a liquid may become the more economical method of transportation. Private industry's plans for large-scale transportation of helium as a liquid and the Bureau's studies in the same general area, coupled with reduced freight rates and larger capacity containers for shipping compressed helium gas, offer good prospects of reducing further the delivered cost of helium. Such reductions will be helpful in making helium more readily available to users.

Despite decades of research, there has been no organized systematic effort directed at learning more about the properties of helium. Work by the Bureau is directed toward filling present gaps in the knowledge of helium's properties to increase its utility. Much of the work is extremely difficult, and years may be required to achieve the desired results.

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INDIUM

By Harold J. Schroeder [1]

INDIUM commercial applications, beginning only 30 years ago as a dental alloy ingredient, have expanded to uses for engine bearings, corrosion-resistant plating, low-melting alloys, transistors, and many other items.

In 1924, 61 years after indium's discovery, the world supply of the metal could have been held in a teaspoon. Then a silverware firm in the United States became interested in the metal for making nontarnishable silverware and began searching for potential sources. It was first found and extracted from Arizona sphalerite, but later a larger supply was found in zinc-plant flue dusts.

Indium has been found in about 50 minerals, but in concentrates too low for any ore deposit to be mined for indium alone. The zinc mineral sphalerite normally contains trace quantities of indium and is the commercial source of the metal. When zinc and zinc-lead ores are processed, indium, if present, remains in various residues, dusts, or in crude zinc and lead, and after many steps in refining, the metal is recovered for commerical use.

One firm in the United States and another in Canada are the only producers of indium in North America. Indium is also produced in several countries of Europe and in Japan. The United States is the largest indium consumer, and in 1957, the peak year, markets were found for almost 20 tons of domestic and imported indium. The United States resource of indium, obtainable as a byproduct in zinc production, is roughly estimated at 320 short tons.

Indium is used principally in electronic devices, in sleeve bearings, and in special alloys for dental casts, fusible safety plugs and links, and solders.

In 1964 quoted prices of indium metal in stick shapes were $2.40 per troy ounce for 30 to 90 troy ounce lots. High purity grades of indium were available at substantially higher prices.

Research on indium in recent years has been centered on the properties of the element and its compounds for specialized uses in the electronics field and improved methods of producing high purity indium for this purpose.

The outlook for indium is for continued growth in the demand for indium and for productive capability adequate to meet the demand.

BACKGROUND

Indium was discovered in 1863 by Professor Ferdinand Reich and his assistant Theodor Richter in Freiburg, Germany, when spectrographic studies for thallium on a sample of sphalerite revealed some undiscovered indigo-blue lines. The newly discovered element was named indium from the characteristic lines of its spectrum, and late that year the metal was isolated.

In 1924, Oneida Community, Ltd., Oneida, N.Y., became interested in indium to make nontarnishable silverware (*5*).[2] In 1926 William S. Murray, now President of the Indium Corp. of America, Utica, N.Y., led a search and found indium at an abandoned prospect, the Beebe property near Kingman, Ariz. About a thousand tons of ore was mined, and 250 ounces of indium was produced. In 1929 a dependable source of indium was found in the Cottrell dusts of a zinc smelter in Montana, and a recovery method was devised. At about the same time a process to use indium for plating other metals was developed. In 1934 an indium alloy for dentistry was made; this was the first commercial use for the element. Since 1934 both the list of uses and total consumption has grown in importance.

[1] Commodity specialist.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

SIZE AND ORGANIZATION OF THE INDUSTRY

The American Smelting and Refining Company, Perth Amboy, N.J., the only producer of indium in 1964 in the United States, began production about 1940. The Anaconda Company, who also began producing indium about 1940, discontinued production after 1960. A number of other firms have produced small quantities of indium but have discontinued the business due to insufficient demand and high recovery cost.

The Consolidated Mining & Smelting Co. of Canada, Ltd., Trail, British Columbia, has produced indium since 1941, and Cerro de Pasco Corp., La Oroya, Peru, from about 1945 until 1951 when production was discontinued. Production of indium also has been reported in the following countries: West Germany (Duisburger Kuperhütte, Duisburg; Dr. W. Franke, Frankfurt a.M.; and Unterharzer Berg und Hüttenwerke, G.m.b.H., Goslar); Japan (The Dowa Mining Co., Mitsui Mining & Smelting Co.; Mitsubishi Metal Mining Co., Ltd., and Toho Zinc Co.); and the U.S.S.R.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Indium is a soft, slippery, silvery-white metal and can be deposited on harder metals by rubbing. Some of its other properties are: Density, 7.31 g./cc.; Brinell hardness, 0.9; melting point, 156.6°C; boiling point, 2,075°C; tensile strength, 380 p.s.i.; specific heat, 0.058 cal./g./°C; and crystal structure, face-centered tetragonal (*1*, *10*).

Indium is placed with boron, aluminum, gallium and thallium in Subgroup III B of the periodic table. It displays a valence of both one and three with three being most common. Indium dissolves slowly in cold dilute acids and more readily in hot dilute or concentrated acid; it is not normally reactive with boiling water or alkalies although when finely divided it forms the hydroxide on contact with water.

Indium is usually considered to be nontoxic, but under certain conditions it is toxic (*2*, *11*). Laboratory experiments on toxicity using animals have been conducted. Underskin injections of indium in quantities from 7 to 30 milligrams per kilogram of body weight and venous injections of indium are toxic. Large quantities of indium hydroxide swallowed over a period of 2 weeks are harmful. Acid foodstuffs containing indium from indium-coated containers showed some absorption of the element by the body. Indium citrate of chloride injected under the skin produced intoxication, and degenerative changes occurred in the liver, kidneys, and heart.

TECHNOLOGY

Mineralogy and Occurrence

The earth's crust contains about 0.1 gram of indium per ton, about the same abundance as silver. It is not found free in nature but has been detected in many minerals. No deposits are rich enough to mine for indium alone. Indium has been found in about 50 minerals, some of which are sphalerite, cassiterite, chalcopyrite, coal, galena, hematite, pyrite, and wolframite. In the United States indium is found in very small quantities in various ores of copper, lead, molybdenum, vanadium, and zinc (*3*, *5*).

Indium is most frequently associated with zinc, and as a result commercial recovery is predominately a byproduct in the processing of zinc-bearing ores. In the metallurgy of zinc, indium, if present, may appear in variable proportions in any of the following products: Flue and Cottrell precipitators dusts, residues from zinc retorts, rejects from zinc sulfate solution at lithopone plants, residues from cadmium recovery, lead blast furnace slags and crude zinc and lead.

Extraction

Numerous methods have been used for the extraction of indium from the several smelter products (*4*, *7*, *8*, *9*).

In one process developed for the recovery of indium, zinc oxide fume recovered from lead blast furnace slag is leached with dilute sulfuric acid to remove the bulk of the zinc, leaving indium in the leach residue. After settlement in a thickener, the residue is leached in stronger sulfuric acid to dissolve the indium. After clarification, indium is precipitated from this solution by the addition of zinc oxide and sodium bisulfite. The indium precipitate is washed with water and then leached with strong sodium hydroxide solution followed by a water wash to remove excess caustic. The precipitate is then washed with dilute sulfuric acid to remove residual zinc. The indium precipitate is then dissolved in strong sulfuric acid, and heavy metals are removed with hydrogen sulfide. Aluminum is added to the clarified pure indium sulfate solution to precipitate an indium metal sponge that may be melted and cast into bars of crude metal. Alternatively the sponge may be purified further by dissolving in hydrochloric acid, followed by precipitating the sulfates with barium chloride and the remaining residual heavy metals with hydrogen sulfide. Indium may be recovered by

precipitation with aluminum or by electrolysis of the purified solution. The sponge or cathode metal is melted under a cover of caustic and cast into market shapes.

Another method recovers indium from crude lead containing zinc and indium as impurities. A first step in this process is to treat a molten bath of the crude metal with a suitable chlorine supplying agent to remove the zinc and indium as a chloride slag. This slag is leached with dilute sulfuric acid, and indium is precipitated as a sponge with zinc dust. The zinc-indium sponge is melted, and zinc is removed with chlorine. The crude indium is melted, cast into anodes, and refined electrolytically.

A complex method is employed at one plant to reclaim indium from the insoluble residue produced during leaching zinc oxide for the electrolytic zinc process. This residue is delivered to the lead smelter for the recovery of contained lead and residual zinc. In the lead blast furnaces, the indium enters the lead bullion and the blast-furnace slag in about equal proportions. From the slag, it is recovered along with zinc and lead during slag-fuming. The fume is leached for the recovery of zinc, and indium again remains in the residue, which is retreated in the lead smelter. From the lead bullion, indium is removed in the bullion dross. The dross is re-treated for recovery of copper matte and lead, and in this process a slag is recovered which contains lead, tin, and copper as the major constituents, together with 2.5 to 3.0 percent indium. The dross re-treatment slag is reduced electrothermally to produce a bullion containing lead, tin, indium, and antimony, which is treated electrolytically to yield a high (20 to 25 percent) indium anode slime. The anode slime is treated chemically to give a crude indium metal, which is then refined electrolytically.

In the distillation process of producing zinc, most of the indium remains with the crude zinc and then follows the lead removed as an impurity during refining. The indium is recovered by first cupeling the lead to increase the indium concentration in the resulting litharge product, then leaching with dilute sulfuric acid, and collecting a crude indium sponge by use of zinc slabs. A refined product is obtained by dissolving the crude indium in sulfuric acid, removing impurities by cementation on strips of indium and also on an indium—cadmium—zinc alloy, followed by collection of pure indium sponge on aluminum strips.

Indium can be recovered from old plating solutions. In this process the solution is first evaporated and the organic material destroyed by ignition. The contained silver, lead, copper, cadmium, zinc and nickel are separated from the residue by successively acidifying, filtering out the insolubles, neutralizing the filtrate, and recovering a precipitate of indium, iron, and tin hydroxide. The hydroxides are dissolved in hydrochloric acid, and the indium recovered by electrolysis.

USES

The three largest uses for indium are in semiconductor devices, in bearing alloys, and in special alloys (*1*, *8*).

The largest single use of indium is probably in transistor devices. In the germanium transistor, indium discs or spheres alloyed to each side of a germanium wafer comprises the heart of the device. The indium imparts desirable modification of the electronic properties and equally important it readily wets and alloys with the germanium at a low temperature resulting in easy fabrication, minimal impurity pickup, and absence of contraction strains. Because of these characteristics indium also is used to solder the lead wires to the device. Considerable research and development is underway to utilize indium antimonide, indium arsenide, and indium phosphide in semiconductors of the intermetallic type.

A continuing large use for indium is in sleeve-type bearings where the element gives dependability and long life to heavy-duty and high-speed bearings. It can be plated on or alloyed with silver-lead, copper-lead, and cadmium alloy bearings surfaces to make them harder, stronger, more corrosion resistant, and more retentive of an oil film by increasing wettability.

Indium is used in many special alloys. Despite its softness, small quantities of the metal harden and strengthen aluminum, lead, and beryllium-copper. Lead-indium alloys, highly resistant to corrosion, are used in chemical processing equipment. Low melting indium alloys are used in surgical casts, foundry patterns, and fusible safety-plugs or links. Indium has been used as an oxygen scavenger in gold dental alloys. It increases the tensile strength and ductility of gold and improves its resistance to tarnish. Indium is used as an ingredient in many solders and brazing compounds. Some indium is used in jewelry and silverware alloys to keep metals bright. Indium alloys capable of wetting glass are used in making glass-to-glass or glass-to-metal seals. A silver-indium-cadmium alloy has been used for a nuclear reactor control rod.

Small experimental uses of indium include its use as an additive in gasoline to increase mechanical efficiency and give cooler running engines. It is also used in heavy-duty lubricants. Indium mirrors reflect all colors of the spectrum, and indium foil can be used to detect radioactivity. Batteries smaller than a penny

using a positive terminal of indium were developed for electronic watches that can operate at constant voltage for 2 years. The oxide is used in glass to give colors ranging from canary yellow to tangerine orange. An electric current passed through a tin-bearing indium oxide film on aircraft windshields prevents fogging and icing.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Indium supply is dependent on zinc production along with other associated byproducts, such as cadmium, gallium, germanium, and thallium, which are recovered in the reduction of zinc ores.

ALTERNATE MATERIALS

Substitutes for indium to prolong bearing life and combat corrosion are difficult to find. A less costly lead-tin overlay is an alternate to lead-indium bearings, but the antiseizure properties and service are not as good as in lead-indium bearings. The change from piston to jet-driven aircraft eliminates need of any engine bearings and is obviously a factor in indium demand. Extensive research underway in the transistor field could lead to entirely new materials replacing the germanium-indium type of transistor. For some uses, such as in dental alloys and in sealing glass joints, gallium can be substituted for indium; however, gallium is costlier than indium.

RESERVES

The indium content of the measured and indicated zinc reserves in the United States is roughly estimated to be 320 short tons. The content of indium in zinc minerals from different deposits varies widely but an average value of 0.0024 percent indium in zinc concentrates has been used as a guide for approximating world reserves.

SOURCES OF STATISTICAL INFORMATION

Statistical information on indium is limited since the relatively few companies in the world recovering indium do not allow publication of production or shipments data. Data on imports and exports of indium are not available because no separation is made of indium figures from those of other miscellaneous materials.

PRODUCTION, CONSUMPTION, AND TRADE

Markets were found for an estimated 20 tons of domestic and imported indium in the United States in 1957, the peak year. Data on the consumption pattern in the past year, however, is not available. More indium was produced in the United States in 1957 than in any previous year. The Anaconda Company publicized it produced 87,600 troy ounces of indium in 1956. Producers shipments were last published in 1951 and were given as 153,000 troy ounces.

Canadian production is large and in 1957, the last year the figures were published, output was 384,000 troy ounces. Most of Canada's output has been exported to the United States, the United Kingdom, and other European countries. The Peruvian production, discontinued after 1951, amounted to 40,000 troy ounces in 1948 and was mostly exported to the United States.

The tariff on indium metal was decreased from 11 percent to 10.5 percent on June 30, 1958. Indium in concentrate can enter the United States duty-free.

STRATEGIC CONSIDERATION

The United States is the major world consumer of indium. Its current and projected needs are fulfilled by domestic production plus substantial imports, principally from Canada. Indium is not on the Government's list of strategic and critical materials for stockpiling.

PRICES

E&MJ Metal and Mineral Markets quoted the following declining prices per troy ounce of 99.9 percent pure indium: $30 to $15 in 1942, $15 to $10 in 1943, $10 to $7.50 in 1944, $7.50, $4, $3, to $2.25 in 1945, and $2.25 since 1945. In 1958 standard grade indium (99.97 percent) was quoted at $2.25 per troy ounce in small quantities to as low as $1.25 per troy ounce for lots of 5,000 or more ounces.

Effective October 1, 1964, prices for indium metal advanced 15 cents per troy ounce, and the new quotes were $2.40 per troy ounce for 30 to 90 troy ounces for stick shapes; in ingot shapes prices were $1.95 per troy ounce for 100 ounce lots and $1.65 per troy ounce for 10,000 and up lots.

High-purity grades of indium were available at substantially higher prices.

TAXES

No special taxes are imposed on the indium industry. Depletion allowance for domestic producers of indium metal is 15 percent.

RESEARCH

A bibliography of more than a thousand scientific references on indium was published for the period 1863–1958 (*5*).

Research on indium by producers has consisted largely of developing and improving metallurgical recovery processes, investigating the element's properties, expanding old uses, and developing new uses.

The Atomic Energy Commission sponsored research work on the indium isotopes and also on the aqueous chemistry of the element.

Recent research on indium has stressed investigation of properties and techniques in the use of indium for semiconductor and other electronic applications. Companion research has been conducted on methods of producing high-purity indium and its compounds.

OUTLOOK

The outlook is for a continued growth in the demand for indium, particularly in electronic uses. Production capabilities appear adequate to meet the anticipated demand.

PROBLEMS

A major problem is the limited and erratic market for indium, largely caused by the relatively few uses comprising a substantial part of total consumption. There is a need to develop the numerous minor and potential uses of indium.

The paucity of published information on production data, practices and efficiencies hampers determination of the potential productive capacity. In a like manner the absence of consumption data makes a market analysis difficult. From a technologic standpoint there is a need for more data on the corrosion of indium and its alloys in various atmospheres and liquids.

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IODINE

By William C. Miller [1]

IODINE was discovered about 150 years ago in solutions leached from the ashes of seaweeds. In 1868, Chile began commercial production of iodine as a byproduct of the nitrate industry. Later it was discovered in California waste oil-well brines and this source now supplies a substantial part of the iodine consumed in the United States.

Iodine occurs in the nitrate deposits of Chile as the minerals lautarite and dietzite. Concentrations of sodium iodate in the nitrate leach solution are treated with sodium bisulfite to precipitate elemental iodine. In California iodine is liberated from oil-well brines by chlorination and blown from the brines by air.

In Michigan iodine is extracted from natural brines by chlorination and blown from the brines by an air-water vapor. In Japan iodine is recovered from brine by the cuprous iodine, electrolytic, or active carbon methods.

The sole domestic producer furnishes about one-fourth of the U.S. requirements. The remainder is imported from Chile and Japan. Iodine and its compounds have many and varied uses in medicine, agriculture, and industry. The use of radioactive iodine in medicine and industry has increased in the past few years. Consumption of iodine is expected to increase owing primarily to expanding use in medicine and pharmacy. The use of iodine as a disinfectant in swimming pools could develop into a sizeable market.

Problems confronting the iodine industry are the lack of data concerning domestic resources, the relatively high cost of producing iodine, and the need for additional markets for iodine and its compounds.

BACKGROUND

Iodine was discovered about 1811 by Bernard Courtois, a potassium nitrate producer. France, unable to obtain from foreign sources the potassium nitrate required for gunpowder, was starting a domestic industry to furnish its requirements. Courtois used crude soda ash obtained from seaweed in his process. He found that an unknown substance introduced with the crude soda ash could be precipitated as a black powder, which yielded a violet vapor when heated. The noted chemist, Gay-Lussac, studied the properties of the powder more intensively and recognized it as a new element. He named it iode, from the Greek word violet color (*5*).[2]

The importance of iodine in medicine was established in 1819 when Dr. Coindent, a Swiss physician, used it as a remedy for goiter. In 1829, wounds were being treated with tincture of iodine. The first application of iodine in the treatment of battle wounds probably occurred during the American Civil War.

By the middle of the 19th century iodine's importance to chemistry was established. Its value was recognized in research and analytical chemistry as a laboratory reagent.

One of the earliest commercial applications of iodine was in 1839 when iodine vapor was utilized as a sensitive material in photography. In 1851 the wet plate process was introduced which used silver iodide (*7*).

For many years the commercial source of iodine continued to be the ashes of seaweed harvested along the coasts of France and Scotland. The seaweed industry declined following 1868 because iodine production from the nitrate deposits in Chile began.

The United States produced some iodine from Pacific coast seaweed during World War I. Recovery of iodine from oil-well brine began in 1928 at a plant in Shreveport, La., and a year later from oil wells in the Signal Hill District of Long Beach, Calif. In 1932 the Louisiana plant was closed and operations moved to California. From 1932 to 1960 U.S. production of iodine was concentrated in California. Iodine from natural brines was produced from wells in the Midland, Mich., area.

[1] Commodity specialist.
[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

In the United States, The Dow Chemical Co., the only primary producer, extracts iodine from waste oil-well brines at Seal Beach, Calif., and from natural brines at Midland, Mich. U.S. production supplies about 25 percent of the domestic demand. In addition to Dow Chemical there are 40 domestic firms that convert crude iodine to resublimed iodine or iodine products.

Chile produces a large part of the world's iodine supply from nitrate (caliche) deposits. These deposits are in the provinces of Antofagasta and Tarapacá on the eastern slope of the coast range in a desert area. The Anglo-Lautaro Nitrate Corp., produces about 90 percent of Chile's iodine. The remaining 10 percent is supplied by several small independent producers.

In the Chiba peninsula, east of Tokyo, Japan, iodine is produced from brines associated with natural gas. Six firms extract iodine in significant quantities. Plants of the following companies are on the Chiba peninsula: Aioi Industrial Co., Ltd., Nipp Development Co., Ltd., Nippon Natural Gas Industry Co., Ltd., Ise Chemical Industry Co., Ltd., and Chiba Iodine Co., Ltd. The Daiichi Pharmaceutical Co., Ltd., operates a plant in Niigata Prefecture. Aioi Industrial Co., with two plants, is the largest producer. The iodine industry is represented by the Brine Iodine Association, a Tokyo trade association, reportedly controlled and financed by the Aioi Industrial Co.

Iodine has been recovered from brines in Indonesia, Java, France, England, Germany, and U.S.S.R. and from seaweed along the coasts of Ireland, Scotland, France, Japan, Norway, and U.S.S.R. The Indonesian production facilities previously owned and operated by Dutch firms which exported iodine presumably are now operated by state firms exclusively for domestic needs.

DEFINITION OF TERMS, GRADES, SPECIFICATIONS, AND PROPERTIES

The minimum purity of commercial crude iodine is normally 99 percent; however, much of the commodity is 99.5 percent pure. Crude iodine sold by domestic producers averages 99.8 percent purity. Impurities are chiefly water, sulfuric acid, and insoluble material. The U.S. Pharmacopoeia XIV specifies an iodine content of not less than 99.8 percent. Resublimed iodine is usually 99.9 percent pure.

Iodine is the only halogen that is a solid at room temperature. It is a gray to purplish black crystalline material, melting at 113° C and boiling at 185° C. The element sublimes readily. Iodine is soluble in water, aqueous iodine solutions, solutions of chlorides, bromides and other salts, and many organic solvents. The element is very active chemically, but is normally less violent than other halogens. Iodine is a better electrical conductor than bromine or chlorine. It forms compounds with all of the other elements except the inert gases, sulfur, and selenium. The element reacts with hydrocarbons to form iodo compounds. Iodine adds to unsaturated compounds to form polyiodo compounds.

Iodine and its more concentrated solutions are classed as poisons because of their irritating effects on the gastrointestinal tract and lungs. Maximum safe concentration for short exposure is set at 0.5 to 0.1 ppm, and at 0.1 ppm for prolonged exposure (*7*).

TECHNOLOGY

Iodine is widely distributed, occuring in small quantities in rocks, soils, brines, and sea water. It occurs in about a dozen different minerals, the most important being lautarite [$Ca(IO_3)_2$], and dietzite ($7CaI_2O_6 \cdot 8CaCrO_4$). Iodine has been recovered commercially from salt deposits, seaweed, and from natural and oil-well brines and brines associated with natural gas.

In Chile, iodine occurs in the caliche or nitrate deposits as the minerals lautarite and dietzite. The iodine content of the deposit ranges up to 0.3 percent; however, the average crude caliche ore contains 0.03 to 0.05 percent iodine in the form of iodates of calcium, potassium, and sodium.

The iodate compounds are dissolved with the nitrate in either the Shanks or the Guggenheim methods used in the processing of the caliche ores. The iodates gradually build up in the mother liquor to a concentration of between 5 and 10 grams per liter of iodine. To recover the iodine a portion of the leach solution is drawn off intermittently and treated with sodium bisulfite to reduce the iodate to iodine. Next an exactly calculated volume of the mother liquor is added and solid iodine is precipitated. The iodine is filtered, washed, pressed into cakes, sublimed in iron retorts, and collected from ceramic condensers in the form of purple-black crystals averaging about 99.6 percent in purity. Iodine recovery plants are operated in such a way as to balance production against expected

sale volume, because their productive capacity exceeds demand (*1*).

In the United States, iodine occurs in oil-well brines of the Los Angeles basin, California and the natural brines of the Midland area, Michigan.

The brines of the Los Angeles basin average about 65 ppm iodine (*7*). The extraction process used by the Dow Chemical Co. is continuous. The brine is acidified with sulfuric acid, treated with chlorine, and pumped to a tower where the iodine is blown out by a countercurrent of air. The iodine vapor is absorbed in a solution of hydroiodic and sulfuric acid and treated with sulfuric dioxide to reduce the iodine to hydroiodic acid. Part of the solution is drawn off and chlorinated to precipitate iodine which is filtered off. It is then melted in a kettle under concentrated sulfuric acid and cast into pigs.

Brines of the Midland area have about one-half of the concentration of the oil-well brines of California. The extraction process for lean iodine brines is similar to the process used for stronger brines and is part of an overall operation that recovers a variety of other products. The brine is acidified with hydrochloric acid and then chlorine is added to partially oxidize the iodine to its elemental form. The oxidized brine enters the top of an iodine desorption tower where the solution moving down the tower is stripped of iodine by a countercurrent stream of air and water vapor. Additional amounts of iodine are formed by the reaction of residual iodine and the ferric ion in the brine as the solution passes through the tower. From the desorption tower the brine goes to other recovery processes. Sulfur dioxide is added to the water-vapor and air phase to reduce the free iodine to the more easily recovered hydrogen iodine form before vapor enters a hydrogen iodine absorber. In the absorber tower, hydriodic and sulfuric acids are added to absorb the hydrogen iodine contained in the carrier gas. From the tower the absorber liquor goes to a batch chlorinator where the iodine is precipitated as crude iodine and is separated from the liquor by filtration. To purify the crude iodine it is melted at about 250° F under a layer of concentrated sulfuric acid. Organic contaminants are decomposed and water is removed by the hot acid (*4*).

In Japan, brines associated with natural gas have replaced seaweed as the principal source of iodine. The brines occur in three sandy strata, underlying the Chiba peninsula, that range in thickness from 625 to 1,640 feet and contain about 25 percent brine.

In the three methods employed to extract the iodine from the brines, the natural gas is removed from the brines at the beginning of the process. In each method the gas is used in the final stage to resublimate the iodine. One method is to introduce iron sulfate and copper sulfate into the brine to produce copper iodide. The iodide is oxidized to yield crude iodine. In another method sulfuric acid is mixed with the brine to yield chlorine gas. To the resultant solution, sodium nitrate is added to precipitate crude iodine which is absorbed by inactive carbon. The crude iodine is dissolved in hot sodium hydroxide and then treated with sodium nitrate and chlorine gas to precipitate refined iodine. In the third method the electrolysis of a mixture of brine and sulfuric acid produces crude iodine. Activated carbon is utilized to absorb the iodine. To refine the crude iodine, the same procedure used by the preceding method is employed.

Iodine has been recovered from seaweed, which extracts it selectively from sea water. In one process, kelp was leached with water and the resulting mother liquor treated with sulfuric acid and manganese dioxide to release iodine. Other processes involved leaching a portion of the iodine by washing fresh seaweed with water and inoculating the slurry with bacteria to cause fermentation. The resulting solution was neutralized with lime, filtered, and evaporated to obtain iodine.

USES

Iodine and iodine compounds have numerous and various uses in medicine, agriculture, and industry. More than half of the iodine consumed is used in medicines and antiseptics. Probably the best known is the household antiseptic, "tincture of iodine." Iodophors, mixture of iodine and organic carriers, are being used increasingly as antiseptics and disinfectants. Iodine and its compounds are used for disinfecting drinking water. Another application is in iodized salt, which contains about 1 part of potassium iodide to 10,000 parts of salt. Silver iodide crystals have been used to seed clouds thereby inducing rainfall. Iodine is essential for the health of man and animals, inasmuch as it promotes the production of thyroxin in the body and thereby prevents goiter. Potassium or sodium iodide, potassium iodate or cuprous iodide are often added to livestock feed. Iodized proteins in stock and fowl feeds prevent various diseases and increase the yield of milk and eggs. Iodine is used in X-ray contrast mediums and in a radioactive isotope (I–131) as a diagnostic aid in examinations of the human body. Radioactive iodine is also used for physical therapy. Iodine–131 is being used in increasing quantities in industry to con-

trol processes and for research. Iodine compounds are used extensively in wet-plate photoengraving and in photographic film emulsions and developers. An expanding use in metallurgy is in the production of high purity metals such as titanium, silicon, hafnium, and zirconium (*9*). In addition, iodine has many other uses in metallurgy, rubber, dyes, analytical reagents, and as catalysts. Potassium iodide has been shown to be an effective disinfectant for swimming pool water which could develop into an important market (*2*).

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

In Chile iodine is recovered as a byproduct of the nitrate industry. Production of iodine is controlled by economic conditions and policies affecting the nitrate industry. In the United States, iodine is obtained as a byproduct of the oil industry and as a coproduct of natural brines. Concentrated liquors from a plant adjoining Searles Lake, Calif., have a relatively high iodine content. Production of iodine from this source may became commercially feasible. In Japan, natural gas is obtained as a coproduct in the production of iodine. The gas is used in the resublimation of the iodine, but some is discarded.

ALTERNATE MATERIALS

Iodine and iodine compounds are relatively high priced commodities whereas other less expensive halogens, such as chlorine or bromine, are substituted where feasible. Some substitutes for iodine compounds used as antiseptics are mercurochrome and antibiotics.

SECONDARY SOURCES AND RECOVERY

In most applications iodine and iodine compounds are consumed in such a way that it is impractical to recover them. Some iodine is recovered in industrial processes, but this quantity is small. At this time secondary recovery is considered an unimportant factor in the economic picture.

RESERVES

Indicated reserves and potential future resources of iodine in domestic oilfield and natural brines are large but have not been adequately measured. Concentration of iodine in oilfield brines near Shreveport, La., averages about 35 ppm and in the Los Angeles basin of California ranges from 60 to 70 ppm. In the natural brines of the Midland, Mich. area the cencentration of iodine is about 35 ppm.

There are large resources of iodine in foreign countries. An estimate of the indicated reserve of Chilean nitrate minerals from which iodine is obtained as a byproduct is about 1 billion tons. The run of mine iodine content of these minerals is about 0.04 percent.

Natural-gas-well brines of Japan are reported to contain about 500,000 tons of iodine. Unmeasured quantities of iodine are contained in brines in Indonesia, Italy, East and West Germany, France, England, and U.S.S.R., as well as saline well water in Java and various coals in West Germany. Seaweed found along the coasts of Ireland, Scotland, France, Japan, Norway, and U.S.S.R. can be considered as a potential reserve.

CONSERVATION

Development of a more efficient recovery method to obtain iodine from Michigan brines with low-iodine concentrations utilizes a portion of a natural resource previously wasted.

In Chile, much of the iodine in the nitrate leach solution is eventually discarded. This iodine could be recovered if there were a larger market.

In some metallurgical processes iodine is recovered and reused. Recent developments in the medical and pharmaceutical fields show a trend toward the use of more efficient preparations having lower iodine contents.

SOURCES OF STATISTICAL INFORMATION

Bureau of Mines obtains data from industry on production and consumption of crude iodine and iodine products. The Bureau also compiles foreign trade data from the Bureau of the Census. Statistical information is published in the Minerals Yearbook and in other statistical and technical publications.

PRODUCTION, CONSUMPTION, AND TRADE

Domestic recovery of iodine from well brines was started in 1928 near Shreveport, La., and in 1929 iodine was extracted from oil-well brines at Long Beach, Calif. Output from the Los Angeles basin area had a pronounced effect on the American market, and by 1936 the price had dropped to an alltime low. Domestic iodine recovery increased slowly after World War II

reaching a peak in 1952. Thereafter output decreased slightly until 1957 and 1958, when it decreased noticeably owing to the sharp drop in the price of crude iodine. In 1960 Dow Chemical became the sole domestic producer. Production was concentrated in California until 1961 when Dow Chemical started production from the natural brines of Michigan. In 1963 increased production capacity for extracting iodine from the natural brines shifted 53 percent of the production to Michigan.

Most iodine consumed in the United States is in the form of iodine compounds. The principal compounds are potassium and sodium iodide although many other inorganic and organic compounds are consumed as shown in table 1. Most crude iodine is resublimed to greater purity or converted to iodine compounds.

The United States imports a large portion of the iodine consumed from Chile and Japan in the form of crude iodine as shown in table 2. Production of crude iodine in Chile is shown in table 3. Large stocks of iodine are held by producers in Chile and by importers near New York City. The latter stocks are replenished at irregular intervals as they become depleted by withdrawal for domestic consumption and small export requirements.

Crude iodine is admitted free of duty under U.S. tariff laws. A charge of 10 cents per pound is levied on resublimed iodine and 25 cents per pound on potassium iodide.

TABLE 1.—*Crude iodine consumed in the United States*

Compound manufactured	1959–61 (average)			1962			1963		
	Number of plants	Crude iodine consumed		Number of plants	Crude iodine consumed		Number of plants	Crude iodine consumed	
		Thousand pounds	Percent of total		Thousand pounds	Percent of total		Thousand pounds	Percent of total
Resublimed iodine	4	113	5	8	106	4	7	150	5
Potassium iodide	10	1,086	53	11	1,079	43	11	1,018	38
Sodium iodide	4	[1]	[1]	5	[1]	[1]	4	[1]	[1]
Other inorganic compounds	17	444	21	24	774	31	21	910	34
Organic compounds	26	427	21	27	538	22	24	617	23
Total	[2] 45	2,070	100	[2] 45	2,497	100	[2] 43	2,695	100

[1] Included with "Other inorganic compounds" to avoid disclosing individual company confidential data.
[2] Nonadditive total because some plants produce more than 1 product.

TABLE 2.—*Crude iodine imported for consumption in the United States, by countries of origin*

[Thousand pounds and thousand dollars]

Year	Chile		Japan		Total	
	Quantity	Value	Quantity	Value	Quantity	Value
1954–58 (average)	1,207	$1,231	419	$534	1,626	$1,765
1959	1,243	892	223	191	1,466	1,083
1960	1,420	1,011	474	414	1,894	1,425
1961	1,964	1,822	1,053	1,030	3,017	2,852
1962	2,229	2,054	797	787	3,026	2,841
1963	2,462	2,093	874	865	3,336	2,958

Source: Bureau of Census.

TABLE 3.—*Production of crude iodine in Chile*

Year	Thousand pounds	Year	Thousand pounds
1954–58 (average)	2,495	1961	4,753
1959	2,443	1962	5,176
1960	3,915	1963	4,063

STRATEGIC CONSIDERATIONS AND GOVERNMENT PROGRAMS

In the United States the only domestic producer supplies about one-fourth of the requirements. Production could be expanded to provide for increased domestic needs, but not for an emergency. Chilean producers could provide ample supplies during an emergency, but the long shipment by water could become critical during wartime.

Iodine, an essential commodity during a war, is stockpiled by the U.S. Government. The basic stockpile goal was completed March 31, 1959. An increase in the stockpile objective was announced in March 1964. On June 30, 1964, Government inventories totaled 4.3 million pounds, of which 3.0 million was in the national (strategic) stockpile, 0.3 million in Commodity Credit Corp. stocks, and 1.0 million in the supplemental stockpile.

PRICES AND COSTS

For many years crude iodine sold for $4 per pound at New York City in accordance with prices established by the Chilean Producers' Association. Prices were reduced after 1931 owing to competition from iodine recovered from California waste oil-well brines. On October 10, 1936, crude iodine sold for 81 cents per pound in New York City. In 1942, the Office of Price Administration placed a ceiling price of $1.28¼ per pound on crude iodine (150-lb. kegs). On November 10, 1946, the ceiling price on crude iodine was removed and the price rose to $1.42½ per pound. According to the Oil, Paint and Drug Reporter, prices during 1963 were as follows:

	January through August	September through December
Crude iodine, in kegs, per pound	$1.10	$1.18
Resublimed iodine, United States Pharmacopoeia (U.S.P.), bottles, drums, do	2.20–2.22	2.20–2.22
Ammonium iodine, National Formulary (N.F.), 25-pound jars, do	4.51	4.51
Calcium iodide, 25-pound jars, do	4.27	4.27
Potassium iodide, U.S.P. drums:		
500 pounds or more, do	1.15–1.55	
Over 500 pounds, do		1.15
Under 500 pounds, do		1.20–1.55
Sodium iodide, U.S.P., 300-pound drums, do	2.13	2.13

TAXES

The U.S. income tax law grants iodine producers, domestic and foreign, a percentage depletion allowance of 15 percent of gross income not to exceed 50 percent of the net income without depletion deduction.

TRANSPORTATION

Cardboard containers, lined with Saran plastic, are used to ship domestic crude iodine. Each container holds 200 pounds of crushed crystalline iodine. Iodine is shipped by train or truck to warehouses in St. Louis, Mo., or New York, N.Y. There is no specific freight classification; it is shipped as "Chemicals, not otherwise indexed by name (n.o.i.b.n.)" and requires no special label. Resublimed iodine is also shipped in cardboard containers, in 25-pound glass jars, and in ¼-, 1-, and 5-pound bottles.

RESEARCH

Research has been done on various aspects of iodine by the iodine industry and research institutions. The Chilean Iodine Educational Bureau, Inc., 120 Broadway, New York, N.Y., has made numerous grants for exploring the advantages of iodine over other halogens as a disinfectant for swimming pool water (*2*). The Bureau of Mines has conducted research on fundamental properties of iodine and on its use in metallurgy.

OUTLOOK

The short-term outlook for domestic production of iodine is for a continued yearly increase. Although the dwindling production of iodine from the oil-well brines of California will concentrate the domestic production of iodine from the brines in the Midland, Mich., area; production from the oil-well brines is expected to continue for several years. Domestic production could not supply an adequate quantity of crude iodine if a very sharp increase in the demand for iodine occurs. The long-term outlook for domestic production is problematical because accurate estimates of iodine reserves are not available. Extraction of iodine from the brines

of Searles Lake, Calif., brines from other areas in Michigan other than Midland, and from sea water may provide potential future resources.

Both the short- and long-term outlook for iodine consumption in the United States is for a steadily increasing commercial use of iodine preparations as disinfecting and sanitizing agents. The use of iodine as an antiseptic and disinfectant will increase because of the growth in population and the additional approval given by Federal, State, and local organizations. Iodophors and diatomic iodine solutions are used as water purifyers in hospitals and restaurants, and as disinfectants in dairies. A prediction was made that the total number of swimming pools would increase by 15 percent by the end of 1964 and that by 1975 there will be approximately 1 million swimming pools in the United States. The treatment of swimming pool water with iodine may develop into an important commercial application for iodine compounds. Advances in process technology and a price level which is more favorably competitive with other halogens, especially chlorine, could result in increasing the consumption of iodine for industrial applications. Increasing use of radioactive iodine in medicine and industry can be expected.

PROBLEMS

Domestic iodine operations are hampered by relatively high costs compared with the foreign areas that supply major tonnages to the present market.

The lack of domestic iodine reserve data prevents firm evaluation of long-range and emergency production potential.

The relatively high cost of producing iodine is a deterrent to its wider utilization. The iodine industry is confronted with the lack of a market commensurate with the production potential.

More detailed statistical and economic data are needed for evaluation of market potential.

Lack of sufficient information on the physical and chemical properties of iodine and its compounds retards the development of new markets.

The principal domestic iodine recovery method makes discarded brine unsuitable for recharging oil-bearing rock strata.

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IRON

By Horace T. Reno [1]

THE IRON ore industry of the United States grew from an annual output of less than 5 million tons in 1870 to over 115 million tons annually in 1951. Since 1951, annual output measured in terms of usable ore shipped to the consumer has declined to about 80 million tons a year, but the industry has continued to grow in terms of capital invested and crude ore mined. There have been sweeping changes in almost every facet of the iron ore industry since World War II when the domestic industry ceased to be the sole source of ore and mining of low-grade magnetite taconite deposits was started in the Lake Superior district.

Sixty-eight countries of the world reported iron ore production in 1963, and more than 150 million tons of iron ore was sold outside the country of origin in 1962.

Sedimentary hematite deposits of primary origin, hematite and magnetite deposits of complex origin, and replacement vein deposits have been the most productive commercial iron deposits to date. However, Precambrian metamorphosed sediments, such as taconite deposits of Minnesota, the jaspilite deposits of Michigan, and the specular hematite and magnetite bearing iron formations which comprise the southern ranges of the Labrador-Quebec district are the principal type of deposits to be newly exploited in the last decade.

Open-pit mines produce approximately 90 percent of the iron ore in the United States because the cost of underground mining precludes expending funds for beneficiation to meet stringent market requirements.

Iron ores are beneficiated by crushing, sizing, washing, concentrating, and agglomerating. Concentration is accomplished by washing, by gravity separation in jigs, heavy-media cyclones, or Humphrey spirals, by magnetic separators, or by flotation. The ores are agglomerated principally by pelletizing at or near the mines and by sintering with other material at steel mills.

Blast furnaces have proved to be the most efficient tool for smelting iron ore and are used to smelt more than 93 percent of the iron ore consumed in the United States. Small furnaces have proved uneconomic principally because of the cost of labor. Coke is the most expensive material and the largest single cost item in iron ore smelting. Methods have been devised to save coke by injecting various gases, oils, and powdered coals into the smelting zone of the furnace.

Sponge iron processes in which the ore is reduced at temperatures below the fusion point of iron, and direct iron processes in which the ore is reduced at temperatures slightly higher than the fusion point, present possible alternative methods for producing iron, but they have been found to be applicable only in specific economic and physical environments. They are not used in this country because they cannot compete in production costs with blast furnaces.

Iron ore resources are reasonably well distributed around the world and unquestionably are sufficient for centuries. The United States uses between 120 and 125 million tons or more of iron ore a year. Most of it is smelted to produce iron, but small quantities are used in making cement, special high-density concrete, and pigments, and magnetite concentrate is used for the heavy-medium in coal processing plants.

Iron is obtained as a coproduct or byproduct in smelting copper, lead, zinc, and nickel sulfides and is a coproduct in mining and treating titanium minerals. The supply of scrap iron and steel fluctuates directly with the demand. Unrecoverable iron losses from the mines through the complete cycle of use to return scrap range from 16 to 31 percent.

The United States emerged from the era of peacetime self-sufficiency and high-grade iron ore in the latter part of the 1940's. In an emergency, however, the United States could be self-sufficient for 2 or 3 years.

[1] Commodity specialist.

Available iron statistical data present adequate coverage of the iron ore industry through the blast furnace. Industry, some States, educational institutions, and the Federal Bureau of Mines are conducting comprehensive iron ore research programs.

The outlook for the iron ore industry throughout the world is that the long-term trend in the price of iron ore in terms of constant value dollars will be downward, and that government actions will not influence the industry adversely. U.S. production for internal consumption will be 80 million tons of 60 percent iron ore by 1970 and 92 million tons by 1980. In addition 5 to 10 million tons will be produced for export. The principal iron mines of the world producing for international trade will have capacity to produce about 300 million tons of high-grade iron ore annually by 1980.

The principal problem of the domestic iron ore industry is to meet both price and quality competition from foreign producers.

BACKGROUND

The iron ore industry of the United States is almost three and one-half centuries old. High-grade ore was produced in the Colonies and smelted in charcoal reduction plants distributed from Georgia to New Hampshire. Incomplete records indicate that less than 50 million tons was mined through 1870. The industry grew from an annual output of less than 5 million tons in 1870 to more than 50 million tons annually by 1910; it was producing 75 million tons annually by 1916, 100 million tons annually by 1942, and over 115 million tons by 1951. Since then the annual output of usable ore has declined to less than 80 million tons, but in terms of capital invested and crude ore mined the industry has continued to grow.

Discovery of the Lake Superior iron mining district and development of the Bessemer steelmaking furnace in the 1850's and the smelting industry's change from charcoal to coal and then to coke in 1875 consolidated iron ore mining and smelting. In the same period, development of the Great Lakes transportation system led to establishment of the world's foremost iron and steel complex in the bituminous coal region of Pennsylvania, Ohio, West Virginia, and Illinois. Iron and steel plants based on local ores were established in Alabama, New York, New Jersey, Tennessee, and Colorado, but the Lake Superior district has accounted for about 80 percent of the iron ore mined in the United States.

Until the end of World War II, the domestic iron-ore mining industry was virtually the sole source of iron ore for the United States. Enriched ores of the Lake Superior district that contained 50 to 55 percent iron, were the accepted standard of high quality by which other ores were gaged. In fact, the industry was little changed from the pattern established 75 years before. The end of the war, however, marked two significant changes: First, the industry ceased to be the sole source of ore for the United States and second, mining of low-grade magnetic taconite deposits was started in the Lake Superior district. As a result there have been sweeping changes in almost every facet of the iron ore industry. Foreign iron ore deposits supply about a third of U.S. needs for ore. Iron ore pellets, a processed product containing at least 63 percent iron, have become the standard of high quality. Most domestic underground iron mines have been shut down and open-pit iron mining has changed from a seasonal to a year-round operation. Only the Great Lakes transportation system and the preeminence of the Lake Superior district remain of the prewar iron mining industrial pattern.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Each year, the iron ore industry produces more than 500 pounds of iron ore for every person in the United States. In 1963, iron ore accounted for more than one-third the value of all the country's metal production. More than 21,000 men were employed directly in the industry; investment per man directly employed has exceeded $100,000 if the costs of transportation facilities are included in the total.

There were 179 iron mines in the United States in 1963; 31 of these produced more than 1 million tons each and together they produced 78 percent of the crude ore and 71 percent of the usable ore; 23 mines produced more than 500,000 tons; 61 produced more than 100,000 tons and the remaining 64 produced less than 100,000 tons. Integrated iron and steel companies control 70 to 80 percent of the domestic iron ore output. Several of the larger of these companies control or have an interest in iron mines in Canada, Chile, Liberia, Peru, and Venezuela.

Sixty-eight countries of the world reported iron ore production in 1963, but 10 countries produced four-fifths of the total. The U.S.S.R. was the leading producer, followed by the United States, France, China, Canada, Sweden, United Kingdom, India, West Germany, and Venezuela in that order.

International trade in iron ore is a large and growing business. In 1962, more than 150 million tons of iron was sold in the world markets outside the country of origin. Conservatively, this ore was valued at the port of export at more than $1 billion. That same year, 19 countries exported more than 1 million tons of ore. Measured by iron content, Canada, shipping mostly to the United States, was the principal exporter, closely followed by Sweden, shipping to Western European countries, and the U.S.S.R., shipping to its satelites. Australia and some of the smaller countries on the west coast of Africa are rapidly expanding their capacity to produce iron ore for export. If world trade in iron ore expands at the growth rate of the last 5 years, it will be more than doubled by 1980.

The Lake Superior district (Michigan, Minnesota, and Wisconsin) accounted for 77 percent of the crude and usable ore produced domestically in 1963; the Northeastern district (New Jersey, New York, and Pennsylvania) accounted for 7 percent of the crude and usable ore; the Western States (Arkansas, Idaho, Missouri, Montana, Nevada, New Mexico, Utah, and Wyoming) accounted for 5 percent of the crude and 6 percent of the usable ore; the Southeastern States (Alabama and Georgia) accounted for 4 percent of the crude ore and 3 percent of the usable ore; and Tennessee, Arizona, Arkansas, California, Colorado, New Mexico, and Texas accounted for 6 percent of the crude and 7 percent of the usable ore. Distribution of iron blast furnaces in the United States is given in table 1.

TABLE 1.—*Location of U.S. iron-blast furnaces, 1964*

Plant location and operating company	Number of stacks
PITTSBURGH-YOUNGSTOWN DISTRICT	
Kentucky:	
Ashland: Armco Steel Corp	3
Ohio: (Youngstown area):	
Campbell: Youngstown Sheet & Tube Co	4
Hubbard: Valley Mould and Iron Corp	1
Warren: Republic Steel Corp	1
Youngstown:	
Republic Steel Corp	5
United States Steel Corp	4
Youngstown Sheet & Tube Co	2
Total	17
Ohio (central and south):	
Canton: Republic Steel Corp	1
Jackson: Jackson Iron & Steel Co	1
Massillon: Republic Steel Corp	1
Middletown: Armco Steel Corp	1
New Miami: Armco Steel Corp	2
Portsmouth: Detroit Steel Corp	2
Steubenville: Wheeling Steel Corp	5
Total	13
Pennsylvania (western) (excluding Pittsburgh area):	
Aliquippa: Jones & Laughlin Steel Corp	5
Erie: Interlake Iron Corp	1
Farrell: Sharon Steel Corp	2
Johnstown: Bethlehem Steel Co	6
Midland: Crucible Steel Co. of America	3
Monessen: Pittsburgh Steel Co	3
Sharpsville: Shenango, Inc	2
Total	22

Plant location and operating company	Number of stacks
PITTSBURGH-YOUNGSTOWN DISTRICT—Con.	
Pennsylvania (Pittsburgh area):	
Braddock: United States Steel Corp	6
Clairton: United States Steel Corp	1
Duquesne: United States Steel Corp	5
McKeesport: United States Steel Corp	4
Neville Island: Shenango, Inc	2
Pittsburgh: Jones & Laughlin Steel Corp	6
Rankin: United States Steel Corp	6
Total	30
West Virginia:	
Weirton: Weirton Steel, Division of National Steel	4
Total, Pittsburgh-Youngstown district	89
CHICAGO DISTRICT	
Illinois:	
Chicago:	
Interlake Iron Corp	2
International Harvester Co	3
Republic Steel Corp	1
United States Steel Corp	11
Youngstown Sheet & Tube Co	3
Granite City: Granite City Steel Co	2
Total	22
Indiana:	
East Chicago:	
Inland Steel Co	8
Youngstown Sheet & Tube Co	3
Gary: United States Steel Corp	12
Total	23

TABLE 1.—*Location of U.S. iron-blast furnaces, 1964*—Continued

Plant location and operating company	Number of stacks
CHICAGO DISTRICT—Continued	
Minnesota:	
Duluth: United States Steel Corp	2
Total, Chicago district	47
CLEVELAND-DETROIT DISTRICT	
Michigan:	
Dearborn: Ford Motor Co	3
River Rouge: Great Lakes Steel Corp., Division of National Steel	4
Trenton: McLouth Steel Corp	2
Total	9
Ohio (Lake area):	
Cleveland:	
United States Steel Corp	2
Jones & Laughlin Steel Corp	3
Republic Steel Corp	6
Lorain: United States Steel Corp	5
Toledo: Interlake Iron Corp	2
Total	18
Total, Cleveland-Detroit district	27
EASTERN DISTRICT	
Maryland:	
Sparrows Point: Bethlehem Steel Co	10
New York:	
Buffalo:	
Hanna Furnace Corp	4
Republic Steel Corp	2
Lackawanna: Bethlehem Steel Co	7
North Tonawanda: Tonawanda Iron Division	1
Troy: Republic Steel Corp	1
Total	15
Pennsylvania (eastern):	
Bethlehem: Bethlehem Steel Co	5
Fairless Hills: United States Steel Corp	3
Sheridan: Lavino & Co., E. J	[1]1
Swedeland: Alan Wood Steel Co	2
Total	11
Total, Eastern district	36
WESTERN DISTRICT	
California:	
Fontana: Kaiser Steel Corp	4
Colorado:	
Pueblo: The Colorado Fuel & Iron Corp	4
Utah:	
Geneva: United States Steel Corp	3
Ironton: United States Steel Corp	2
Total	5
Total, Western district	13
SOUTHERN DISTRICT	
Alabama:	
Birmingham:	
Republic Steel Corp	2
United States Pipe & Foundry Co	2
Ensley: United States Steel Corp	5
Fairfield: United States Steel Corp	3
Gadsden: Republic Steel Corp	2
North Birmingham: United States Pipe & Foundry Co	1
Woodward: Woodward Iron Co	4
Total	19
Tennessee:	
Lyles-Wrigley:	
Merritt-Chapman & Scott Corp.: Tennessee Products & Chemical Corp	1
Rockwood: Woodward Iron Co	2
Total	3
Texas:	
Houston:	
Sheffield Division of Armco Steel Corp	1
Lone Star: Lone Star Steel Co	1
Total	2
Virginia:	
Lynchburg: Lavino & Co., E. J	[1]2
Total, Southern district	26
Total all districts	238

[1] Ferromanganese only.

Source: American Iron and Steel Institute.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Iron ore is classified according to the principal mineral constituent as either hematite, magnetite, or limonite (brown ore). In the Southeastern district hematite ore is called red ore. The term "natural ore" is used to designate iron ore that contains moisture, in contrast to "dry ore" that has been dried but not calcined. Iron ore is measured in long (gross) tons to the blast furnace, but pig iron, the blast furnace product, is measured in short (net) tons.

Iron ores are described as crude or usable. Crude ore is the material, as mined, prior to any processing for removing waste constituents, though it may be crushed and screened. Usable ore is the product of mine, beneficiating, or

agglomerating plant which is shipped without further processing to the consumer. In this category are included direct-shipping ore (the usable ore as mined), iron ore concentrate (ore from which waste constituents have been removed), and iron ore agglomerate (compact masses of either ore or fine-grained concentrate).

Beneficiated ores are usable ores that have been treated to improve either their physical or chemical characteristics. Thus ores that have been improved by simple sizing or crushing are among the beneficiated ores.

Grades of iron ore are established according to percentage and type of impurities and by physical characteristics; within limits, the percentage of iron is a secondary consideration. Iron ore delivered to Lake Erie ports is purchased on the basis of 51.5 percent iron; usable iron ore shipped in the Southeastern district in 1958 contained an average of 39 percent iron.

The five principal grades of iron ore are—(1) bessemer, containing not over 0.045 percent phosphorus; (2) low-phosphorous, nonbessemer, containing between 0.045 and 0.180 percent phosphorus; (3) high-phosphorous, containing over 0.180 percent phosphorus; (4) manganiferous, containing over 2 percent manganese; and (5) siliceous, containing over 18 percent silica. In addition, iron ore is often described as lump, fine, high sulfur, high silica or titaniferous. Buyers' specifications are rigid within the above named grades, and maximum impurity limits are always cited.

TECHNOLOGY

Geology

The iron content of the earth's crust has been calculated at 5.06 percent (*13*).[2] A fractional part of this iron has been concentrated, under varying geologic conditions, into widely distributed, multi-origin deposits formed in many rock types. Of the various commercial deposits, the most productive to date have been: (1) sedimentary hematitic deposits of primary ore enriched by weathering processes; (2) hematite and magnetite deposits of complex origin in metamorphic rocks; and (3) replacement and vein deposits.

Limonite, siderite, hematite, and magnetite are the principal iron-ore minerals. In sedimentary deposits these minerals have been deposited mechanically, chemically, or biochemically; the mineral species have been governed by the conditions of deposition. The iron was derived from weathering of igneous minerals such as hornblende, pyroxene, or mica. Silicate, aluminate, and carbonate minerals, and iron and titanium mineral combinations thereof are common gangue.

Precambrian metamorphosed sediments comprise a major part of the world's low-grade iron-ore deposits. They were exploited first in Lake Superior district after World War II as a result of (1) imminent depletion of high-grade deposits, (2) growing demand for iron, and (3) development of more efficient mining and beneficiation techniques. The taconite deposits of Minnesota in which magnetite is the principal iron mineral and the jaspilite deposits of Michigan in which specular-hematite is the principal iron mineral have been proved commercial sources of iron only since 1954. The success of the mining companies exploiting these deposits, and the demand for the iron-ore pellets produced from them influenced others in the iron ore industry to prospect for and develop similar deposits. Precambrian metamorphosed specular-hematite and magnetite bearing iron formations which comprise the southern ranges of Labrador-Quebec district in Canada have been developed on a large scale in the last decade, and similar deposits have been developed recently in the Western United States and in the U.S.S.R.

Titaniferous iron deposits of sedimentary metamorphic, and magmatic origin are prevalent throughout the world, but few are exploited where other type iron deposits are available.

Mining

Open-pit mines produce approximately 90 percent of the iron ore in the United States. The trend has been toward more open-pit mining and less underground mining because improvements in excavating equipment has permitted a steady increase in the overburden-to-ore ratio since World War II. In the last 5 years, however, underground mining has been decreasing steadily because the average ore as mined underground would not meet rigid market specifications, and the cost of underground mining precluded expending funds for beneficiation. Underground mines produced approximately 15 million tons of ore in 1963. It is significant that only 16 million tons of direct-shipping ore was produced in 1963.

Open-Pit Mining

Mining methods in open-pit iron mines are similar but vary widely in detail. Overburden is stripped with power shovels, draglines, or scrapers, and is transported either by rail, trucks, conveyor belts, skips, or in the scrapers. The overburden on shallow, thin-bedded deposits often is double or triple cast with a dragline excavator. The choice of equipment is

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

controlled by the physical characteristics of the overburden, the depth and size of the ore body, and the nature of surrounding terrain.

In large pits, ore is loaded exclusively with power shovels, but in some thin-bedded deposits it is loaded with dragline excavators. Ore is transported from the pits by rail, trucks, skips, conveyor belts, or by combinations thereof; the choice with few exceptions is ruled by the grade of haul and the size of operation.

Drilling equipment used in large, open-pit iron mines includes churn drills, rotary drills, down-the-hole drills, jet-piercing apparatus, and air-driven percussion drills. Jackhammers and wagon drills are used in the smaller mines. Churn drills predominate in the Lake Superior district's soft residual-hematite mines, and jet-piercing apparatus predominates in taconite and jaspilite mines. However, roller-cone rotary drills and down-the-hole drills with tungsten-carbide-insert cutting edges have proved superior to churn drills and to jet-piercing equipment in some types of ground.

Mining benches in open-pit mines range in height from 20 to 50 feet; the average is about 35 feet. Drill holes spacing and burden (distance from first line of holes to face) range from 12 to 30 feet. Hole sizes range from 5 to 12 inches. Jet-piercing apparatus make an uneven diameter hole ranging in size from 8 to 20 inches or more. The usual practice is to take advantage of the flexibility to chamber the bottom or various depths of the hole to obtain the most efficient blasting. Field-mixed ammonium nitrate and fuel oil is now the most common explosive used in open-pit iron mines where moisture is not a problem. Waterproof free-flowing low-velocity blasting powders are used in wet ground. Some form of delay detonation is used in all except the smallest open-pit iron mines.

Underground Mining

There has been a concerted effort since 1960 to improve the efficiency and lower the cost of underground iron mining. Raise boring machines, a hard rock mole that drives 7-foot diameter openings, and continuous miners similar to coal mining machines have been used successfully. The larger underground mines have been mechanized to the same extent as the open-pit mines and wherever possible loaders, trammers, conveyors, samplers, and hoists have been fully automated. Closed circuit television is used to monitor isolated operations. These practices have stimulated the underground miners to modify and vary mining methods to the point where conventional nomenclature no longer completely describes the operation.

Sublevel caving has been the principal underground method of mining iron ore in the Lake Superior district. Block and panel caving and variations thereof are used in large ore bodies where dilution is not a problem. Shrinkage stoping, open stoping, sublevel stoping, with many modifications and various other methods also are used depending on the size, shape, and character of the orebody, and the character of the enclosing rocks. Most bedded deposits are mined by room and pillar methods similar to those used in coal mining. Air-driven percussion and auger drills and electric driven auger drills are used in underground iron mines. Drifters on jumbos are used in large headings, jack-leg hammers in small headings, and jack-leg and stopers in stopes and raises. Long holes are drilled with air-driven drifters and rotary machines with auger-type drilling strings.

Ammonium nitrate and fuel oil, ammonium nitrate-TNT slurries, and gelatin dynamites are used in blasting underground. Cap and fuse regular delay and fast delay caps are used for detonation. Slushers are the principal means of loading. Room and pillar mines use conventional metal mine mechanical loaders and some coal loaders. Ore is transported underground on rails, on conveyor belts, and with trackless haulage units.

Beneficiation (30, 38)

Beneficiate, as applied to iron ore, is a broad general term that includes any process used to improve physical or chemical characteristics of the ore, that is any process used to increase the value of the ore after it is mined, but before it is smelted. Thus crushing, sizing, washing, concentrating and agglomerating are processes of beneficiation.

Crushing, Sizing, Washing, and Concentrating

High-grade, hard lump ores are crushed to about 8 inches if destined for use in an open-hearth furnace and a maximum of 4 inches if destined for use in a blast furnace. Within the last few years it has become common practice to remove minus ¼-inch material from all ore sold on the open market. The coarse material then is graded and sized to customer's specifications. Minus ¼-inch material is sold at a discount or agglomerated by one of several processes described later.

Soft, iron-bearing material containing clay and sand in which the iron is concentrated in a coarser and harder portion is beneficiated by washing. The ore is crushed, screened, and then washed in log washers or on screens and in various types of classifiers. In some plants, bowl classifiers are used for separating fine iron minerals from the log washer tailings. From 45 to

70 percent of the iron is recovered in a product ranging from 40 to 60 percent iron. Reject fines from washing plants contain from 10 to 45 percent iron (in extreme instances).

Gravity concentration by jigging or heavy-medium separation equipment is applied to concentrating coarse ore (usually plus ¼-inch and seldom finer than ⅛-inch), and Humphrey spirals, and wet cyclone separators (both with and without suspension medium), are used for concentrating fine ore and the tails from jigs and heavy medium wash plants. Each type of gravity concentration equipment has certain advantages or disadvantages, depending on the physical characteristics of the ore and on the difference in the specific gravity of ore and waste. Heavy medium cyclone separators have high capacity and make a good separation. Humphrey spirals make a better separation of fine material than cyclones, but do not have as high capacity. Heavy-medium units make a sharper, more rapid separation on unsized coarse ore than do jigs. Among the various types of gravity-separation equipment, cyclones (heavy medium) and other types of heavy-medium plants seem to be most favored by the large producers.

Magnetic concentration would present the answer to iron-ore beneficiation if the ores contained only magnetite. Unfortunately, in the preponderance of so-called magnetite iron ore, including the taconites, the iron is distributed in magnetic and nonmagnetic iron minerals and in iron-bearing silicates. Consequently, the overall recovery of a typical magnetic concentration plant ranges from 30 to 95 percent of the iron in the feed. In many instances the tailings contain silicate minerals from which a desirable iron-bearing product cannot be recovered by present methods, but they also contain recoverable iron in the form of oxide minerals.

Essentially all types of magnetic separators have been applied to concentrating magnetite ore, but most operators have settled on the belt units for cobbing and rougher concentration and on drum units for finishing. If the ore is ground finely enough to liberate the mineral constituents, magnetic process plants recover 95 percent or more of the magnetic iron content of the ores in a 62 to 68 percent iron concentrate. The siliceous magnetite iron-bearing formations of the Lake Superior district require grinding to pass 100-mesh (75 to 92 percent minus 325-mesh); not even a 500-mesh grind, however, will liberate iron minerals from materials obtained from some parts of the district's slaty formation material.

The distribution of iron by mineral in the nonmagnetic cherty taconite on the Mesabi range between Grand Rapids and Buhl, Minn., as determined by the Bureau of Mines, is as follows:

Mineral	*Percent of total iron content*	*Range (percent)*
Magnetite	21. 3	0–66
Nonmagnetic oxides	[1] 74. 8	5–100
Siderite	2. 7	0–90
Silicate	1. 2	0–90

[1] By difference.

Magnetic taconites currently mined contain 60 to 70 percent of their total iron in magnetite minerals and the remainder in nonmagnetic oxide and silicate minerals.

Nonmagnetic iron minerals can be concentrated with conventional magnetic separators by converting them to magnetite in a controlled reduction roasting atmosphere in shaft, multiple hearth, or rotating cylindrical furnaces.

Iron ore concentration with high-tension separation equipment that imparts differential movement of mineral particles with a grounded rotor and a concentration of mobile ions was reported in 1957 (*18*). Reportedly the equipment compared favorably with commercial magnetic and flotation separation equipment in semi-pilot plant tests on hematite, magnetite, and martite ores, but it has not yet been applied on a large scale commercially. Nevertheless, electrostatic separators continue to be of interest to researchers seeking profitable methods of concentrating complex iron ores.

The Mines Experimentation Station of the University of Minnesota is conducting a pilot-plant study of a process for beneficiating low-grade Mesabi range ores in which electrostatic and high-intensity wet magnetic separation circuits are used to concentrate part of the iron minerals.

Specular-hematite ores are concentrated efficiently with flotation, and flotation is applied to concentrating the fine-grained hematite minerals in material from which part of the iron minerals have been removed by other methods.

Flotation also has been applied successfully for upgrading iron ore concentrate by floating silica, apatite, and other mineral impurities away from the iron minerals. The art and science of applying flotation to concentrating iron ores has been advanced markedly in the last decade, but reagents and procedures have not been found that are commercially applicable to ores containing mixtures of limonite, goethite, and hematite.

Agglomeration (2, 5, 21, 27)

Fine-grained iron ore and iron ore concentrate is agglomerated before being smelted in a blast furnace by sintering, nodulizing, pelletizing, or briquetting. The fine ore is sintered with heat on traveling grates or in a batch ma-

chine, nodulized with heat in a rotary kiln, pelletized without heat in a rotating drum, pan, saucer, or cone, or briquetted without heat using some form of binder in pressure-roll machines. Hot ore briquetting processes have been successful on a laboratory scale using pressure rolls to form the briquettes, but a 2-year pilot-plant test on Lake Superior fine grained siliceous ore indicated that the operation would not be profitable because of high maintenance costs. Together the several types of materials produced is called agglomerate; individually they are called iron-ore sinter, nodules, pellets, and briquettes. Pellets and usually briquettes are indurated by some form of heat treatment after they are formed. The pellets are treated in updraft or downdraft traveling grate furnaces, in shaft furnaces, or in grate-kiln furnaces. Each method has its advantage. Data are not available to determine which is the better under all circumstances.

Self-fluxing agglomerates, wherein fuels, flux, and iron minerals are combined, present theoretical possibilities for saving in the cost of operating a blast furnace. The principal advantage is that the flux would be calcined before it reached the furnace. Lime sinter, which contains less than enough basic material to neutralize all the acidic materials in the ore, is in common use, but completely self-fluxing agglomerates are still not widely used.

Bureau researchers have produced partially reduced pellets in the laboratory and on a pilot plant scale. Partially reduced pellets are those in which most of the oxygen has been removed from the contained iron oxide minerals. These pellets were proved superior blast furnace feed in the Bureau's experimental furnace, and similar pellets have been tested in commercial furnaces, but the results have not yet been published.

Smelting (1, 22, 24)

Blast furnaces are used to smelt more than 93 percent of the iron ore consumed in the United States, open-hearth furnaces are used to smelt about 6 percent, and electric furnaces producing ferroalloys are used to smelt less than 0.2 percent. Their proportions have been about the same since the turn of the century despite concerted efforts by many researchers to develop alternatives for the blast furnace. The fact is that the blast furnace is the most efficient tool for smelting iron ore yet developed. Its use over more than three centuries has progressed from crude art to highly sophisticated metallurgical technology. Probably more has been done to increase its efficiency in the last 10 years than was done in the preceding 100.

The average blast furnace in the United States is 95 feet high and 23 feet in diameter at the hearth, it has a working volume of 33,200 cubic feet, and will produce about 1,200 tons of pig iron (hot metal) per day. The largest furnace in the United States is the Armco Steel Corporations' "Amanda" at Ashland, Ky. The "Amanda" is 104 feet high, 30 feet 6 inches in diameter at the hearth, has a working volume of 68,510 cubic feet, and capacity to produce 3,340 tons per day. Record monthly production, however, was held in 1964 by the Bethlehem Steel Co.'s "J" furnace at Sparrows Point, Md., with 104,435 tons of iron produced in October 1963. The "J" furnace is 105 feet 3 inches high and has a hearth diameter of 28 feet 9 inches and working volume of 50,522 cubic feet.

Nor is the Amanda the world's largest blast furnace. This distinction is claimed by Tokai Iron & Steel Co. Ltd.'s No. 1 blast furnace at Nagoya Harbor, Japan, which has a hearth diameter of 32 feet 2 inches, working volume of 71,371 cubic feet, and daily capacity of over 3,500 tons.

The smallest iron blast furnace in the United States has a height of 55 feet, hearth diameter of 7 feet, working volume of 3,316 cubic feet, and capacity of about 100 tons per day. It has been used principally to produce ferroalloys but was not operating in 1964.

Small blast furnaces have proved uneconomic principally because of the cost of labor. It takes about the same crew to operate a small furnace as it does a large one. Therefore, there has been an unbroken trend since World War II to build larger furnaces. Apparently the structural limit has not yet been reached as Russian metallurgists have announced plans to build a furnace with a 36-foot hearth diameter and 95,000 cubic feet of working volume.

The chemistry of the blast furnace is extremely complex. At least 27 chemical reactions are possible, but simply stated the furnace performs two functions: (1) it reduces iron oxide to metal, and (2) it fuses the charge so that metal and slag will separate. Coke is the principal fuel and reductant, and limestone and/or dolomite is used for flux. These materials are charged with the ore into the top of the furnace. Coke is the most expensive material, and the largest single cost item in iron ore smelting. Within the last decade, methods have been devised to save coke by injecting part of the fuel and reductant needed into the smelting zone of the furnace. Various gases, oils, and powdered coals have been used successfully for this purpose. Availability and cost determine the choice. Natural gas has been the principal alternative fuel used in the United States. Fuel oil has been the principal alternative in European countries. Theoretically, more coke can be saved using powdered coal, but reliable tech-

niques for injecting the coal were not developed until 1962. Coal injection was reported to the Bureau for the first time in 1963 when 29,303 tons of bituminous coal and some anthracite, 43.9 million gallons of oil, 3.8 billion cubic feet of coke oven gas, and 31.6 billion cubic feet of natural gas were used in blast furnaces.

Blast furnace efficiency is judged by the ratio of fuel consumed to the iron produced. Recovery of the iron in the feed is over 93 percent. Capacity or productivity is related to efficiency and varies widely depending on the quality and characteristics of the charge in addition to depending on the operation of the furnace. Furnace capacities were published until 1960, but the practice was discontinued because the figures were widely misunderstood and misinterpreted. Furthermore, advancing technology made the capacity figures all but meaningless in terms of the metal that could be produced in a given size furnace.

Blast furnace operations have been greatly improved in the last two decades: (1) by grading and sizing the burden (charge without fuel); (2) by increasing the temperature and oxygen content of the blast; (3) by the fuel injection discussed above; (4) by increasing the rate and pressure of the blast; and (5) by using a burden that contains more iron per unit volume. Iron ore pellets have been accepted in the United States as the best material to obtain optimum furnace operation. However, in Europe, sized and graded sinter prepared from high-grade ore is considered superior to pellet by some furnace operators. Relative reducibility, tempered by length of experience with each, probably is responsible for the choice. Use of either high-grade pellet or sinter leads to better furnace operations and their physical and chemical characteristics set the standards by which other iron raw materials are measured.

Theoretically, use of partially reduced pellets will improve blast furnace operation and increase capacity as much as have pellets and sinter. Furthermore, the advantage of using them has been demonstrated practically in the Bureau experimental blast furnace, so there is little doubt that they will be used commercially if their cost is not prohibitive. Preliminary estimates indicate that the cost of iron in partially reduced pellets delivered to most blast furnaces will be little more than the cost of iron delivered in pellets; therefore, partially reduced pellets probably will replace pellets for feed to furnaces in which there is need to increase output. That is, additional iron ore smelting capacity will be obtained by using prereduced pellets, rather than by building new blast furnaces.

Electric-furnace smelting has proved marginally competitive with the blast furnace in areas of inexpensive electricity a long distance from a supply of coke. Almost any carbonaceous material will serve for the reductant in an electric furnace. The Bureau has had marked success with wood chips. Flux requirements are essentially the same as for a blast furnace.

Sponge-iron processes, in which the ore is reduced at temperatures below the fusion point of iron, and direct iron processes, in which the ore is reduced at a temperature slightly higher than the fusion point, present possible alternative methods of producing iron. Scarcity of coke, or in some areas impending depletion of coking coal and high relative prices of coke in others, and changing economic and technologic conditions, often make these processes exceptionally attractive. Periodically since 1910, research institutions and industrial organizations have shown great interest and activity in developing processes to replace blast furnace smelting. A great deal of research effort has been expended on direct reduction possibilities. Several hundred processes have been developed through successful laboratory tests, and a dozen or more have been successfully tested in semicommercial pilot plants. At least five and possibly more are being applied commercially in specific physical and economic environments (*11*, *12*, *23*, *28*).

It is at times impossible to distinguish between semicommercial pilot and commercial operations. Höganäs and Wiberg-Soderfors, true sponge iron processes developed in Sweden, have long records of successful continuous commercial applications in that country. The Krupp-Renn, and "H-Iron" processes, have been applied commercially but in some instances have been found inapplicable with changing economic environments. Since its inception the Hy-L process has been used successfully and continuously to make sponge iron at Monterey, Mexico, and the Echeverria process has been used the same way at Legazpia, Spain. The R–N, S–L, and Strategic-Udy processes have been tested successfully in semicommercial plants and are offered as processes commercially applicable to processing selected iron ores under some conditions. In addition, several fluidized bed processes for obtaining iron from high-grade concentrate have been tested on a large scale. These processes also are offered as commercially applicable under some conditions.

Table 2 presents an elementary comparison of selected direct-reduction processes. The reader is referred to the work of Barrett, of the Bureau of Mines (*4*); Brown, of Jones and Laughlin Steel Corp.; (*7*) and Chase and McBride, of the United States Steel Corp. (*10*) for comprehensive discussion and review of the principal sponge iron and direct iron processes.

TABLE 2.—*Comparison of principal iron ore direct reduction processes*

Item compared	Krupp-Renn	R-N	Strategic-Udy	H-Iron	Hy-L	Echeverria	S-L
Possible ore feed	Low-grade high silica but low in sulfur and phosphorus.	Any-grade lump sulfur and phosphorus not critical.	Any-grade—but ¼ inch or finer Low in sulfur and phosphorus.	High-grade fine	High-grade lump	High-grade lump, sinter, or pellet.	High-grade lump ore or pellets.
Flux	None	Limestone—for sulfur only.	Limestone	None	None	Limestone—for sulfur only.	Dolomite for sulfur only.
Reductant	Solid carbonaceous, fairly low-grade.	Solid carbonaceous, excess recycled.	Solid carbonaceous	Hydrogen	H_2-CO-gas	Solid carbonaceous, excess recycled.	Coal.
Reducing temperature.	1,250° C	982° to 1,093° C	1,100° to 1,300° C	480° C to 538° C	About 1,100° C	1,050° C	1,090° C.
Pressure	Atmosphere	Atmosphere	Atmosphere	400 psig	Atmosphere	Atmosphere	Atmosphere.
Source of heat	Solid carbonaceous, fairly low-grade, or fuel oil.	Oil, gas, or solid burner fuel.	Gas from electric furnace in circuit plus other gas.	Any	Natural gas	Fuel oil, natural gas, producer gas, etc.	Gas.
Equipment	Rotary kiln	Rotary kiln	Rotary kiln Short-arc electric furnace.	Fluidized-bed pressure vessels, at least three.	Four retorts Heat accumulator.	Vertical retort, external heat.	Rotary kiln.
First product	Mixture of slag and luppen.	Mixture of fuel-slag and iron.	Partially reduced ore-flux mixture.	Iron powder with slight impurities.	Sponge, 85 percent iron	Mixture of fuel slag and iron.	Mixture of fuel slag and iron.
Second treatment	Magnetic separation	Gravity separation for fuel then ground, wet, magnetic separation.	Short-arc electric furnace.	Compression mechanism.	None	Screening and magnetic separation.	Screening and dry magnetic separation.
Second product	Iron (luppen)	Iron briquets over 95 percent iron.	Pig iron or semi-steel	Iron chips or powder	None	Sized sponge iron	Sponge iron pellets and briquets.
Apparent advantages.	Low-grade ore Low-cost fuel Iron recovered from silicates.	Flexibility Low-grade ore Low-cost fuel Removes sulfur and phosphorus.	Low-grade ore Produces semi-steel Sulfur and phosphorus can be removed selectively Flexibility.	No trouble with fine concentrate Wide degree of reduction possible Product will replace all or any part scrap and ore charge to steel furnace.	Replaces scrap Most sulfur eliminated.	Replaces scrap Simplicity—small units are efficient Most sulfur eliminated.	Removes sulfur and phosphorus.
Apparent disadvantages and operating problems.	Sulfur and phosphorus remain with iron.	Low recovery in silicate iron mineral ore.	Must have inexpensive source of electricity.	Must have high-grade fine ore Does not remove any contaminants.	Requires high-grade ore and low-cost gas and power.	Must have high-grade ore Does not remove phosphorus.	Process not developed to process low-grade or siliceous ore.
	Ring formation in kiln	None	Ring formation in kiln	No choice of reductants.	Does not remove phosphorus Batch system.	Batch system	None.

The Krupp-Renn process probably should be classified as a beneficiating process rather than a sponge iron process because it has been used almost exclusively to upgrade siliceous ores. It is a rotary kiln process to which fuel ore mixtures are fed to a internally heated kiln. The iron oxides are reduced to metal and the iron gathers in nodules or lumps at the lower end of the kiln. The product is cooled and fed to a ballmill and then to a magnetic separator. The lumps, called "luppen" contain 90 to 95 percent iron. Availability of high-grade ores has made the Krupp-Renn process obsolete in most parts of the world. Krupp-Renn plants are still being operated in Czechoslovakia, but those in West Germany where the process was developed have been shut down or are operating on high-grade ore.

The R-N process is a refinement of the Krupp-Renn process. It also is an internally heated rotary kiln process, but the temperature is carefully controlled so that at no point in the kiln does it exceed the fusion point of iron. The grade and grain-size of ore fed to an R-N kiln are not significant except that retention time becomes excessive if the ore lumps exceed 1½ inches in diameter, or the reduction time is excessive at smaller diameters if the ore is very dense. Limestone or dolomite is added in small quantities to arrest sulfur. The kiln can be fired with either an oil, gas, or solid-fuel burner, and the temperature gradient throughout the kiln is closely controlled by limiting the quantity of air available for combustion. Kiln products are separated by screening, gravity, or magnetic processes; and the unused solid-carbon reductant is cleaned and returned to the circuit. The iron-bearing portion is pulverized and separated magnetically and the iron is pressed into metallic briquets of high strength and density.

The S-L process is essentially the same as the R-N process except that it has been applied only to high-grade lump ore and pellets.

Recognizing this similarity the proprietors of the R-N and S-L processes have agreed to license their joint technology to Lurgi Gesellschaft fur Chimie und Huttenwesen m.b.h. of Frankfurt (Main), West Germany, for an improved direct reduction process, known as the SL/RN process.

The Strategic-Udy process can utilize any grade iron ore, but the particle grain size should be one-fourth inch or less because the economy of the process is dependent on rapid throughput. The ore is partially reduced in a rotary kiln at 1,100° to 1,300° C, and fed directly from the kiln into a short-arc electric furnace. Solid carbonaceous material and gas from the electric furnace partially reduce the ore in the kiln. The solid carbon not used in the kiln is "coked" and passes through to finish reducing the ore in the electric furnace. Limestone or dolomite flux as needed is fed to the kiln with the iron ore.

The Hy-L and Echeverria processes are true sponge iron reductions in that the temperature is never permitted to exceed the melting point of iron and in that the end product is used as is in steelmaking. Both processes require high-grade iron ore or concentrate because all impurities are carried through to the iron end product.

In the Hy-L process, the ore is reduced in four identical reduction reactors each with a capacity of approximately 100 tons of raw ore. The system operates on a 12-hour cycle during which the reactors pass through four stages of 3 hours each. In the first stage, the ore is preheated with hot gas and the reduction process is started. Most of the ore is reduced in the second stage. The remainder is reduced and the charge takes on approximately 2 percent of combined carbon in the third stage. In the fourth stage, the ore, now sponge iron, is cooled and the heat is recuperated and used to preheat the ore in the first stage. The final product is a sponge iron averaging about 85 percent metal from which 85 percent of the sulfur has been removed. The sponge is suitable for use wherever cold iron melting stock is normally employed.

Although the chemistry and metallurgy of the Hy-L and Echeverria processes are similar the mechanics are completely different. Ore in the Echeverria process is charged with any low volatile carbonaceous fuel into externally heated shaft-retorts. A small amount of limestone is mixed to the ore to pick up the sulfur. Retorts are about 10 meters high with a circular horizontal section slightly tapered to permit free descent in the column. The retorts are installed within a refractory-lined oven which is heated by combustion of producer gas. Time from charge to discharge is approximately 48 hours depending on the reducibility of the ore. Each retort has a capacity of approximately 1.4 tons of iron product per day. The product is screened into three sizes and then separated from the excess coal and limestone magnetically. The screened sponge products are used in any cold melting stock operation similar to the Hy-L sponge.

The H-Iron process is a fluidized-bed reduction and therefore requires high-grade, fine-grained iron ore or concentrate. As in the Hy-L and Echeverria processes, most impurities are carried through the process to the end product. The ore is reduced with hydrogen at 480° to 538° C, under 400 pounds per square inch, gage pressure (*31*). The product is an impure iron powder that can be compressed to

form chips suitable for a steel-furnace charge, or the powder can be fed directly into an electric furnace by a method developed cooperatively in Bureau laboratories (*3*).

Electric-furnace smelting of iron ore, and the various sponge-iron and direct-iron processes are not used in most instances in this country because they cannot compete in production costs with the blast furnace, but they have the following advantages that make them attractive in some geographic areas: (1) they would not require as large a capital investment as a blast furnace; (2) impurities, such as sulfur in coke, would not be introduced in the same extent; (3) they apparently can recover iron from complex minerals with a byproduct slag enriched in other metals; and (4) they can afford better product purity control.

USES

Iron ore, in addition to supplying the metal for iron and steel products, is used in paint pigments, cement, basic refractories, as a fluxing agent in nonferrous smelting and as a constituent of some catalytic agents. Lump magnetite ore is used for heavy aggregate in concrete for covering underwater pipelines, as a shielding material in nuclear powerplants, for the medium in jig beds and sink floatplants, and during World War II it was used for ship ballast.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Iron is obtained as a coproduct in the mining of copper, lead, zinc, and nickel in operations whereby iron sulphides are separated from other metal minerals and then roasted to drive off the sulfur, leaving a residue of high-grade iron oxides. The residue, called iron cinder, is sintered to make an iron product which commands a premium price.

Iron is also obtained from the magnetite produced with the mining of titanium minerals, and as a byproduct when titaniferous ores are smelted to recover TiO_2. Magnetic iron minerals are separated in an iron concentrate, and if the concentrate contains too much titanium, it may be blended with other iron-bearing material to form suitable blast-furnace feed.

Many heavy mineral placer concentrates contain some magnetite. If the operation is large enough, and the mine location is favorable, the magnetite is separated and marketed.

Titanium-bearing iron ores are not utilized for blast-furnace feed in the United States at present because under normal furnace operation titanium forms oxide accretions in the bottom of the furnace. Few domestic mineral deposits contain enough titanium to be mined at present for that element alone.

SECONDARY SOURCES AND RECOVERY

Secondary iron is recovered from flue dust, mill scale, and from scrap iron and steel that is unsuitable for steel furnaces. Iron and steel scrap comprises about 50 percent of steel furnace feed and is a raw material often considered vital to the operation of ferroalloy furnaces.

The scrap supply follows the demand, but data have not been developed to predict accurately the supply that will be available under specific circumstances.

Unrecoverable losses of iron from the mine or beneficiation plant through its cycle of use range as follows: Loss in shipments from the mines to the steel mills is believed to be small. Blast-furnace loss ranges from 1 to 1.5 percent in plants that have dust collectors and Cottrell precipitators. Without this equipment, the loss is about 7 percent. Iron loss in ferroalloy and steel furnaces ranges from 2 to 3 percent. In addition to these furnace losses, there is also a loss of about 1 percent, which cannot be accounted for between the feed to the blast furnace and steel mill shipments. Estimates of irretrievable fabricated steel losses range from 12 to 25 percent or more. Thus, total unrecovable iron losses through a complete cycle from mine to use and secondary recovery range from 16 to 36 percent.

RESOURCES

The total resources of iron ore available to industry have increased sharply in recent years, in particular because improved beneficiation can now produce high-grade materials economically from the very abundant low-grade metamorphosed sedimentary iron formations. Formerly only those parts of the iron formations that had been concentrated by natural geologic processes could be used. However, availability of high-grade, physically desirable blast-furnace feed has reduced the demand for certain natural ores, causing substantial shifts in the sources of iron ore.

Resources are unquestionably sufficient for centuries; they are reasonably well distributed around the world, and the major factors to be weighed in selecting particular areas to develop are those of costs (mining, beneficiation, transportation, and taxation), political stability, and security. Nevertheless, very real differences exist in the geologic settings (continuity, thickness, attitude, etc.), which affect mining costs, and in the mineralogy of the ores, which determine the feasibility of economical ungrading.

The resource figures in the following tables were compiled by the Geological Survey from many sources. They are approximations of quantities and grades known to exist in selected areas of the world that are either in exploitation now or for which there is reason to believe that development may take place in the relatively near future. No attempt is made to break them into the traditional measured, indicated, and inferred categories. Most of the material, even of the highest grade, will undergo some form of beneficiation before use; the grade figures give a general idea of the concentration ratio between ore in the ground and the quantity of "usable iron ore" that can be produced.

TABLE 3.—*Iron ore resources of the United States* [1]

[Million long tons]

Region	Quantity	Percent iron	Type
Northeast (New York, New Jersey, Pennsylvania).	300	30–50+	Magnetite.
	1,000	25+	Magnetite, hematite.
Southeast (Alabama, Georgia, Tennessee).	8,000	30–38	Red (hematite) ore.
	50	38–57	Brown (limonite) ore.
Lake Superior (Minnesota, Michigan, Wisconsin).	500	50–54	Direct shipping.
	>100,000	22–30+	Taconite, jaspilite.
South Central (Missouri, Texas).	250	40–60	Magnetite, hematite.
	150	40+	Limonite and siderite.
Rocky Mountain (South Dakota, Wyoming, Colorado, New Mexico, Utah).	500	48–60	Hematite and magnetite.
	2,000	25–40	Taconite.
Northwest (Montana, Idaho, Washington, Oregon).	15	40–60	Limonite, magnetite, hematite.
	1,000	25–40	Taconite.
Southwest (Arizona, California, Nevada).	100	50+	Magnetite.
	2,000	25–40	Magnetite and taconite.

[1] Compiled by Geological Survey, U.S. Department of the Interior

TABLE 4.—*Iron ore resources of selected countries* [1]

[Million long tons]

Country	Quantity	Percent iron
Australia	16,000	55–68
Brazil	2,400	>66
	600	58–66
	25,000	40–58
Canada	4,000	49–60+
	24,000	22–37
Chile	1,000	53–69
France	8,000	30–55
Gabon	900	60–64
	>100	40–45
India	21,600	55–60+
Liberia	400	56–68
	300	37+
Malaya	150	55–60
Mauritania	200	65
Norway	1,600	32–38
Peru	1,000	45–65
Sierra Leone	100	56
	100	48
Sweden	3,500	58–68
U.S.S.R	8,300	>46
	50,000	40–46
	32,700	<40
Venezuela	3,500	52–65
	>300	40–50

[1] Compiled by Geological Survey, U.S. Department of the Interior.

CONSERVATION

If it must be removed from the pit, low-grade iron ore is saved at most open-pit mines by stockpiling it in spoil banks so that it can be recovered when changing technologic or economic conditions make such recovery profitable. A few concentrating plant operators have constructed their tailing ponds so that the tailings can be retreated. Substandard iron ore is mixed with high-grade ore to produce a greater tonnage of usable product if buyer's specifications allow it.

SOURCES OF STATISTICAL INFORMATION

The Bureau of Mines canvasses major iron-ore producers monthly, and all producers annually. These canvasses are conducted in close cooperation with State agencies and industry trade associations. Export and import data are compiled by the Bureau of Mines from records of the Bureau of the Census, Department of Commerce. The Bureau of Mines also compiles iron-ore production statistics for foreign countries from official foreign government publications and from consular reports of the Department of State.

Bureau coverage of the domestic industry is practically 100 percent; mine production figures for small mining operations that fail to report are obtained from consumer's purchase records. Coverage of foreign iron-ore statistics is complete except for the U.S.S.R. and its satellites, and the figures are as accurate as the limited number of mineral attaches in foreign countries permits. The Bureau publishes iron-ore statistics monthly in Mineral Industry Surveys and annually in the Minerals Yearbook.

The American Iron Ore Association publishes monthly Lake Superior iron-ore shipments from United States and Canadian ports, monthly stocks of iron ore and agglomerates at U.S. docks and furnace yards, U.S. and Canadian monthly consumption of iron ore and agglomerates by districts and processes, and an annual statistical report of shipments of Lake Superior iron ore to upper Lake ports and all-rail shipments to consumers. U.S. production of pig iron and steel, with corollary statistics, are published weekly, monthly, and annually by the American Iron and Steel Institute. Together, these statistical data present completely adequate coverage of the iron ore industry through the blast furnace, but beyond the blast furnace many pertinent data on iron production, consumption, and stocks are lacking.

PRODUCTION, CONSUMPTION, AND TRADE

The relative position of the iron producing districts and the changes in quality and the extent of concentration practiced in each are shown in table 5.

The Lake Superior district has been the principal source of domestic iron ore. Its production of crude ore has remained about the same for the last 10 years, while its production of usable ore has declined steadily. The grade of usable ore produced, however, has increased steadily.

TABLE 5.—*Crude and usable iron ore produced in the United States, grade of usable ore, and ratio of concentration, by districts*

Year	Crude ore mined (thousand long tons)	Usable ore produced		Ratio of crude ore to usable ore
		Quantity (thousand long tons)	Grade (percent)	
	Lake Superior district			
1949	79,306	68,494	50.77	1.2:1
1950	96,561	79,627	49.75	1.2:1
1951	115,846	93,947	51.10	1.2:1
1952	94,933	77,095	50.35	1.2:1
1953	120,425	95,655	50.46	1.3:1
1954	80,725	60,994	50.99	1.3:1
1955	109,118	83,255	51.28	1.3:1
1956	110,050	77,817	50.90	1.4:1
1957	122,768	83,530	52.43	1.5:1
1958	84,445	51,777	51.89	1.6:1
1959	74,081	43,950	53.94	1.7:1
1960	125,082	71,792	54.13	1.7:1
1961	105,505	53,207	55.27	2.0:1
1962	111,829	55,556	55.78	2.0:1
1963	117,314	56,132	56.51	2.1:1
	Southeastern district			
1949	11,485	7,602	36.64	1.5:1
1950	11,910	7,508	37.43	1.6:1
1951	14,480	8,587	37.57	1.7:1
1952	12,978	7,624	37.95	1.7:1
1953	11,978	7,692	38.13	1.6:1
1954	10,737	6,150	37.72	1.7:1
1955	11,010	7,106	36.77	1.5:1
1956	11,117	6,035	39.09	1.8:1
1957	12,068	6,749	38.36	1.8:1
1958	5,898	3,827	37.89	1.5:1
1959	8,194	4,350	38.90	1.9:1
1960	7,627	4,365	39.27	1.7:1
1961	6,150	3,539	36.81	1.7:1
1962	7,357	3,186	29.76	2.3:1
1963	6,547	2,419	36.79	2.7:1
	Northeastern district			
1949	8,405	3,864	61.45	2.2:1
1950	9,576	4,475	61.14	2.1:1
1951	10,787	5,181	61.34	2.1:1
1952	10,182	4,426	61.47	2.3:1
1953	12,025	5,162	61.58	2.3:1
1954	9,769	4,084	62.54	2.4:1
1955	11,086	4,650	67.85	2.4:1
1956	11,623	4,867	62.05	2.4:1
1957	12,116	4,962	62.39	2.4:1
1958	8,666	3,412	62.08	2.5:1
1959	9,024	3,669	62.22	2.5:1
1960	11,128	4,125	61.85	2.7:1
1961	9,806	4,048	62.13	2.4:1
1962	11,232	4,584	63.05	2.5:1
1963	11,344	4,922	63.13	2.3:1

TABLE 5.—*Crude and usable iron ore produced in the United States, grade of usable ore, and ratio of concentration, by districts*—Con.

Year	Crude ore mined (thousand long tons)	Usable ore produced		Ratio of crude ore to usable ore
		Quantity (thousand long tons)	Grade (percent)	
	Western district			
1949	5,655	4,442	52.25	1.3:1
1950	7,693	5,861	50.97	1.3:1
1951	10,962	[1] 8,181	53.43	1.3:1
1952	10,158	[1] 8,030	53.82	1.2:1
1953	12,184	8,869	57.98	1.4:1
1954	8,066	6,065	53.60	1.3:1
1955	11,114	6,958	51.83	1.6:1
1956	13,335	8,073	51.68	1.7:1
1957	6,720	6,467	48.93	1.0:1
1958	5,572	5,178	50.24	1.1:1
1959	4,794	4,356	50.76	1.1:1
1960	5,327	4,583	52.19	1.2:1
1961	5,829	4,850	52.78	1.2:1
1962	6,350	4,438	52.79	1.4:1
1963	7,805	4,531	55.21	1.7:1
	Other districts			
1957	7,153	3,630	37.41	2.0:1
1958	5,234	2,764	52.50	1.9:1
1959	6,491	3,160	54.69	2.1:1
1960	5,736	3,127	50.76	1.8:1
1961	9,296	5,007	52.83	1.9:1
1962	6,535	3,485	53.86	1.9:1
1963	9,766	4,838	55.12	2.0:1

[1] Includes 39,219 tons of ore from Puerto Rico in 1951; 138,613 tons in 1952.

The Southeastern district was the second ranked source of domestic iron ore until 1957, but since then its production of crude and usable ore have declined, and in 1963 it produced less than any of the other recognized districts. The tenor of usable ore produced there has remained about the same, but the grade of crude ore mined has declined.

The Northeastern district has maintained its position among the iron ore districts, producing about the same quantity of crude and usable ore. The average grade of usable ore produced in the district has increased slightly in the last decade.

The Western district also has maintained its position while producing an increasingly better grade of usable ore.

The United States uses from 120 to 125 million tons or more of iron ore per year, or roughly 1,300 pounds of iron in ore for each ton of steel produced. Most of it is smelted to produce iron, but small quantities are used in making cement, special high-density concrete, and paint pigments, and magnetite concentrate is used for heavy-medium in coal processing plants.

Iron ore has become a significant part of the foreign trade of the United States as domestic production has fallen steadily, and imports have increased to supplant domestic mines in supplying the country's needs, figure 1.

The chart, figure 2, showing the average grade of imports and the average grade of iron ore produced in the United States in the last two decades provides insight into this competition for the domestic market. It is apparent that the average grade of usable ore produced in the United States ultimately will equal or exceed that of imported ore.

Most of the U.S. foreign trade in iron ore has been with Canada. Venezuela supplanted Canada as the principal supplier for a short time, but considering both exports and imports, iron ore trade with Canada has always been the larger.

From 1960 to 1963 Canada supplied 44 percent of iron ore imports; Venezuela supplied 35 percent; Chile 10 percent; and Peru about 4 percent. Most imported blast furnace ore originates in these four countries. Most of the open-hearth, lump ore originated in Brazil and Liberia, with lesser amounts from Venezuela and Chile.

The United States sells about 5 million tons of iron ore per year to Canada and more than 1 million tons to Japan. Sales to Canada are essentially trades made to cut down the transportation costs in each country.

Iron ore is not subject to tariffs.

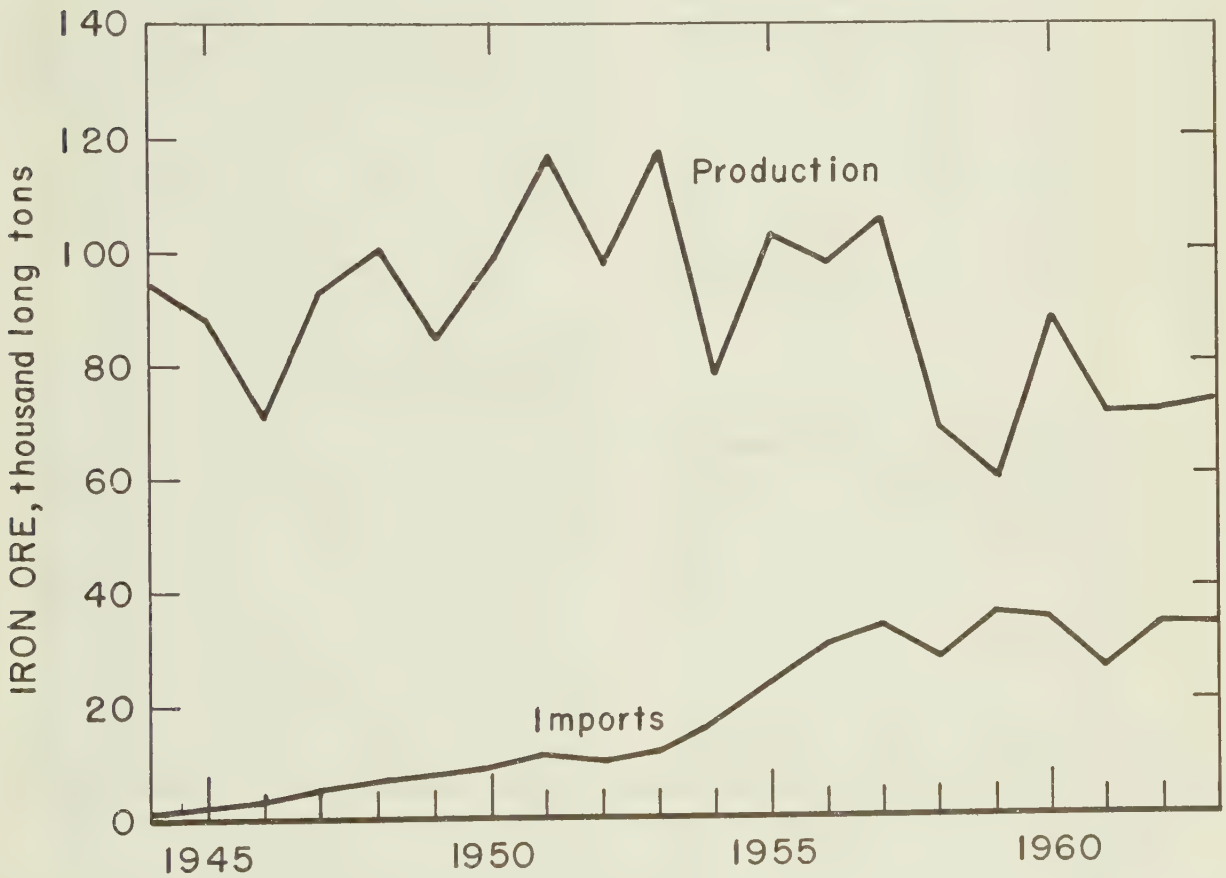

FIGURE 1.—United States Iron Ore Production and Imports for Consumption.

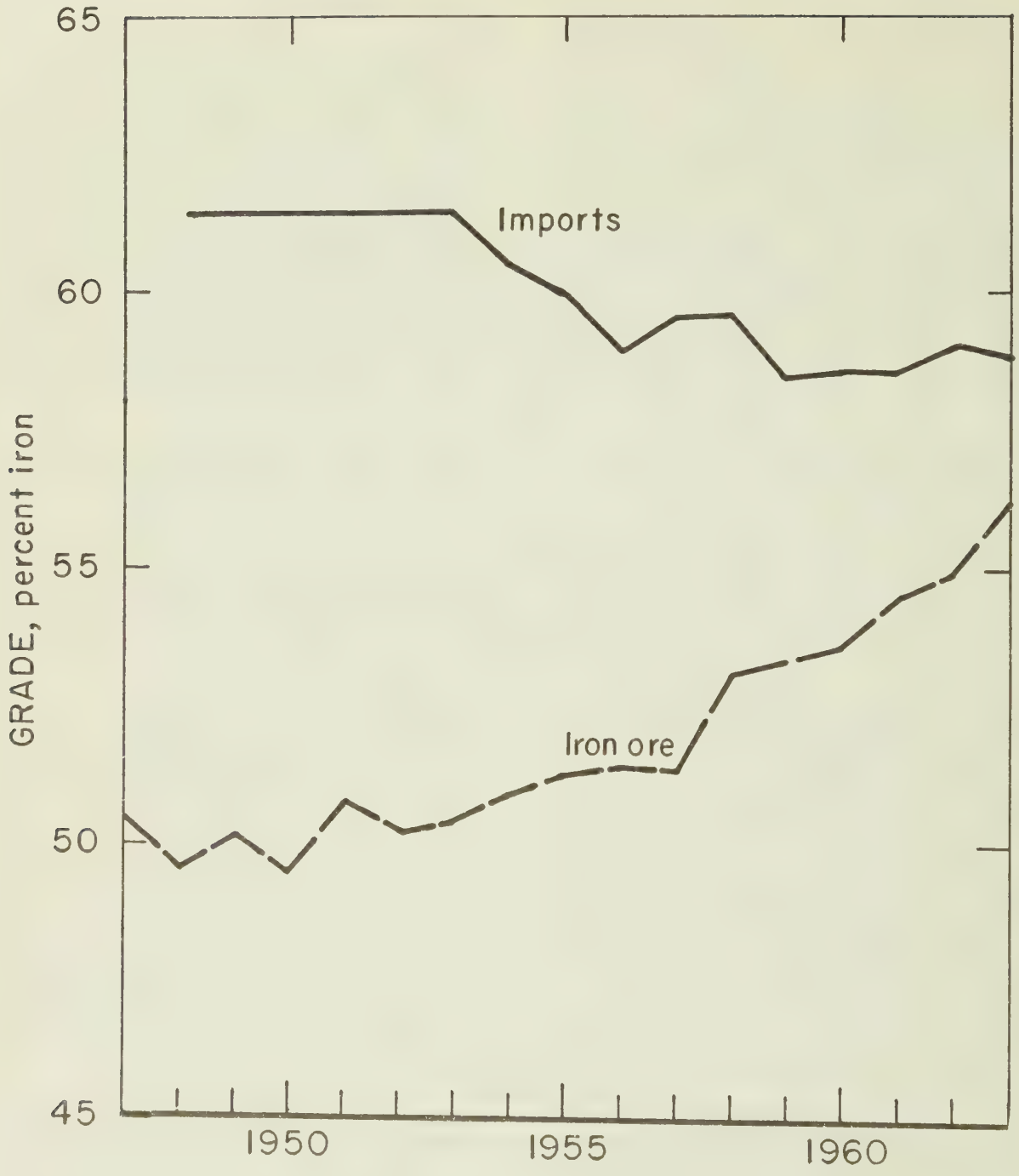

FIGURE 2.—Average Grades of Domestic and Imported Usable Iron Ore Consumed in the United States.

STRATEGIC CONSIDERATIONS

Iron is absolutely essential to the economic well-being and safety of the United States. The principal danger to supply is vulnerability of the transportation system. Most of the Lake Superior district iron ore moves to markets through the Great Lakes, and this movement is essential if the country is to have an adequate supply of iron ore because railroads do not have enough capacity to replace the Lake transportation system. Furthermore, the St. Lawrence Seaway carries 10 to 15 million tons of iron ore annually from Canada to the steel-producing centers on the lower Great Lakes, and the United States is partially dependent on iron ore from South America. Stockpiling iron ore, to date, has been deemed impractical.

The United States emerged from the era of peacetime self-sufficiency in high-grade iron ore about the latter part of the 1940's. In an emergency, however, the United States could be self-sufficient for 2 or 3 years. This does not mean that there is not enough iron ore in the country to supply our needs, only that its geographic distribution is such that the output cannot be easily increased. If ore from Canada were available, the two countries probably could be self-sufficient indefinitely.

GOVERNMENT PROGRAMS

The Defense Production Act of 1950 included provision for government assistance in exploration and development of iron-ore deposits, and the Internal Revenue Act of the same year provided accelerated tax amortization for new and expanded iron-ore production facilities. Iron-ore exploration assistance was continued until May 15, 1953, when it was suspended. It was reactivated again by order of the Secretary of the Interior on July 24, 1961, and is still available January 1965. Rapid tax amortization incentives were continued through September 29, 1955. During the time the expansion goal permitting rapid tax amortization of capital invested in iron-ore facilities was in effect, planned investments under the program totaled over $1.25 billion.

PRICES AND COSTS

Table 6 gives the Lake Erie price for iron ore, 1955–59 average and 1960–64. Lake Erie base prices are established each year by publication of a major contract between a prominent iron ore producer and a steel corporation. Other companies follow this lead and negotiate contracts accordingly. Lake Erie base prices are published each year before the start of the Lake Superior shipping season by several trade journals and by leading mining companies.

Current iron-ore mining costs range from about $2.50 per ton in open pits to $10 or more per ton in underground mines. The average production costs of iron ore produced in underground and open pit mines in Minnesota, 1952–56 average and 1957 to 1961, are given in table 7.

TABLE 6.—*Lake Erie base prices of iron ore, per long ton, 51.5 percent iron, natural*

Year	Old range bessemer	Old range nonbessemer	Mesabi bessemer	Mesabi nonbessemer
1955–59 (average)	$11.44	$11.29	$11.21	$11.06
1960	11.85	11.70	11.60	11.45
1961	11.85	11.70	11.60	11.45
1962	11.05	10.90	10.80	10.65
1963	11.05	10.90	10.80	10.65

TABLE 7.—*Average cost per long ton of mining and beneficiating iron ore in Minnesota* [1]

Year	Development	Labor and supplies	Other [2]	Royalty	Total
1952–56 (average)	$0.625	$0.905	$0.915	$0.433	$2.878
1957	.660	.989	1.145	.474	3.268
1958	.693	.991	1.556	.513	3.753
1959	.757	1.242	1.932	.484	4.415
1960	.755	1.131	1.761	.523	4.170
1961	.787	1.150	2.018	.567	4.522

[1] Bulletin of the University of Minnesota, Mining Directory Issue. V. 66, No. 9, May 1, 1963.
[2] Includes beneficiation.

TAXES

Federal tax laws allow iron-ore miners a 15 percent depletion deduction from gross income to arrive at net taxable income. Direct State taxes are levied on reserves, both developed and undeveloped. In some instances, however, reserve tax laws for low-grade deposits have been relaxed, and now only low-grade ore production is taxed.

EMPLOYMENT AND PRODUCTIVITY

The number of men employed at domestic iron mines and beneficiating plants has declined about one-third since World War II. Employment has been related to usable ore production but has not fluctuated with it directly because mining companies have planned operations to maintain a stable labor force. The mining companies have also kept most men employed year round. These practices have obscured productivity measurements so that year to year comparisons are not signficant. For example, data reported to the Bureau indicates that output per man in 1955 was 1.78 tons of usable ore per hour, and in 1962 it was 1.72 tons per hour.

There is no doubt, however, that the trend in productivity is upward. Output was only 0.75 ton per man-hour in 1923, the first year employment figures were reported to the Bureau.

TABLE 8.—*Employment and productivity at iron ore mines and beneficiating plants*

Year	Average number men employed	Productivity, tons usable ore per man-hour
1925	35,757	.717
1930	30,975	.816
1935	14,987	1.162
1940	25,128	1.512
1945	26,777	1.465
1950	31,087	1.492
1955	29,000	1.78
1960	27,543	1.63
1962	21,010	1.72

TRANSPORTATION

More than 75 percent of the iron ore produced in the United States is transported in ore carriers on the Great Lakes. The Great Lakes' fleet in 1964 numbered 170 vessels. Their average age was 41 years. The quantity of ore that the fleet can move in any one year varies according to the length of the shipping season; the annual carrying capacity under the most favorable circumstances is 76.3 million long tons.

Iron ore transported over the Great Lakes system is transferred a minimum of 3 times (rail, to loading dock, to ship, to railroad) and a maximum of 5 times (mine truck, to railroad, to loading dock, to ship, to stockpile, to railroad). Each transfer generates additional fines that detract from the value of the ore. Blending of ore from various mines to assure a guaranteed analysis is an integral part of the mine-to-rail-to-ship transportation system.

The St. Lawrence Seaway carries over 12 million long tons of foreign iron ore annually to Great Lakes ports of the United States. This ore comes principally from the Quebec-Labrador iron belt of Canada via rail to river ports and thence through the Seaway following a transfer pattern identical to that of ore transported on the Great Lakes system. Seaway locks limit ore carriers to 25-foot 6-inch draft, 700-foot length, and 75-foot beam. Iron ore in transoceanic trade is carried in special bulk cargo ships ranging in carrying capacity from 25,000 to 70,000 long tons. Oceangoing iron ore cargo ships with carrying capacity over 100,000 long tons are being planned.

Iron ore from mines in the Southeastern, Northeastern, and Western States including Texas and Missouri normally moves all-rail to the furnaces, and 1 to 2 million tons annually is transported all-rail from the Lake Superior district. Less than 1 percent of the iron ore produced domestically is moved from mines to furnaces by truck.

Transportation costs of delivering iron ore from mines to the furnaces range from 40 to 50 percent of the value of the ore. In 1963, charges over the Great Lakes system from the Mesabi range to the Pittsburgh Steel district were $6.60 per long ton; and all-rail charges were $10.23 per ton.

RESEARCH

Since World War II, private industry has been heavily engaged in iron research, principally to develop ore dressing techniques for beneficiating the taconites of Minnesota, and the jaspilites of Michigan. The industry supports research laboratories, with a total annual budget estimated at more than $5 million. Total industry expenditure for iron ore and associated research is believed to range between $15 and $25 million annually. The Federal and State annual total is about $1 million.

The Minnesota State Mines Experiment Station at the University of Minnesota has been conducting a small but comprehensive iron-ore research program since 1911.

The Michigan Bureau of Mineral Research was established on the campus of the Michigan College of Mining and Technology in 1955, principally to conduct research projects applicable to the State's iron-ore resources.

The Bureau of Mines has had an iron-ore research program since establishment of Bureau stations at the University of Minnesota in 1917 and at the University of Alabama in 1921. Until World War II, the Bureau's program was conducted without urgency and only to develop basic scientific technical data to expand and develop the base of the country's iron-ore resources, and to encourage development of iron industries in new areas. During the war, the Bureau explored many iron-ore deposits. Since then, the Bureau has been concerned with more immediate problems of increasing domestic iron supply and of devising mining and ore-dressing techniques that would enable profitable exploitation of complex iron-ore deposits. A small hearth, low-shaft experimental blast furnace is operated at Bruceton, Pa., by the Bureau in cooperation with private industry to study material substitution and operating techniques applicable to conservation and development of the Nation's iron resources.

OUTLOOK

The iron ore industry will be a vital part of the expanding industrialization brought about by rising living standards and a growing population. New mines will be opened to share in the markets created by the iron and steel industries now being planned for the recently independent, less developed nations. Others will be opened to help supply the demands foreseen for industrial areas now in existence. Those mines producing high-grade, low-silica pellets or equivalent will tend to capture the world markets. When most of the existing blast furnace capacity using high-grade pellets is utilized, partially reduced agglomerates will tend to supplant the pellets. That is when more blast furnace capacity is needed, it will be obtained through use of partially reduced agglomerates in preference to building more furnaces.

Technology will continue to exert strong influence on the course of the iron ore industry. Except in unusual circumstances, iron ore will be mined in open pits from the large low-grade, easily beneficiated deposits. The trend toward larger equipment and automation of transportation and crushing plants will continue. Drilling and blasting practices in the taconite mines will improve but not at the fast rate of the last decade.

By 1970 essentially all iron ore produced for consumption by the industrialized nations will be beneficiated. The conventional gravity and magnetic separation and flotation ore dressing processes will be refined and used more in series or combinations to produce a higher-grade product with decreasing silica-alumina limits. Electrostatic separation and roasting to obtain iron minerals susceptible to magnetic attraction probably will be applied commercially within the next decade.

Pelletizing will continue to be the preferred method of iron ore agglomeration in the United States and will be used more in other countries, but it will not replace existing sintering plants. Partial reduction in conjunction with pelletizing will be applied increasingly. However, researchers eventually will find a method to bypass the agglomeration process so that fine grain concentrate can be used directly to produce iron.

General economic and political activities probably will have little effect on the structure of the domestic iron ore industry, but production and transportation relative costs will trend downward. Common market countries may regulate the iron and steel industries to some extent but, other than in Luxembourg and the Lorraine district of France, competition eventually will force establishment of a free iron-ore market in Europe.

The outlook for economic and political activities related to the world iron-ore industry is that the long-term trend in the price of iron ore in terms of constant value dollars will be downward, and that future government actions will not adversely influence the industry and in some instances will actually favor it.

Worldwide capacity to produce iron ore probably will continue greatly to exceed requirements. Nevertheless, many mining districts now supplying ore to restricted markets may not have capacity to supply all ore of the grade and quality needed.

Mine capacity is distinguished from probable production which is related to but not numerically identical to requirements. In North America mine capacity to produce high-grade agglomerates in the United States will increase steadily. The Lake Superior district will continue to be the principal source of domestically produced iron ore. The district's capacity to produce high-grade taconite pellets will reach 30 million tons annually by the late 1960's and 40 to 50 million tons by 1980. By then the district also will have capacity to produce 10 million tons of high-grade pellets annually from semitaconite or soft ores. The district's capacity to produce direct shipping ores and the conventional 51 to 60 percent iron-ore concentrate probably will decrease rapidly through the next 5 years, and may be only 5 to 10 million tons by 1980. Capacity to produce these conventional ores in the Lake Superior district will be fixed by the domestic steel industy's need for flexibility in output.

The Northeastern district including Pennsylvania probably will maintain capacity to produce at least 6 million tons of high-grade iron ore agglomerates annually until 1980, although new deposits will have to be developed to do so.

The Southeastern district's productive capacity probably reached bottom when most of the underground mines in the Big Seam of the Clinton formation were shut down in 1959. Capacity to produce 3 to 5 million tons annually more than likely will be maintained in the southeast through 1970, but unless technology develops, competition from foreign operations will close most of the mines within the next few years.

Iron-ore productive capacity in the Western district, which includes Missouri, will expand to keep pace with Western markets, probably reaching 14 million tons annually within 5 years. It is just a question of time before the large

low-grade iron resources of Arizona, Nevada, and Montana are exploited on a large scale. Even assuming no radical change in technology or in transportation costs, it is expected that at least one deposit in each of these States will be producing ore by 1975. If transportation costs can be halved, deposits in South Dakota probably will be exploited for the Eastern market.

Alaskan iron ore deposits may be exploited for export to Japan or for local use. In either case their impact on the world's iron ore industry will not be significant.

Accordingly, it is expected that United States iron ore production for internal consumption will be 80 million tons of 60 percent iron ore by 1970 and 92 million tons by 1980. In addition 5 to 10 million tons will be produced annually for the export market.

Canadian iron ore productive capacity without doubt will be expanded at a rate to supply all the iron ore the U.S. and Canadian markets will absorb. In addition, Canadian ore will be mined for export to both Asiatic and European markets. The Japanese probably will continue to buy ore from Canada at a rate commensurate with other trade between the two countries. Japan bought 1,545,000 tons of Canadian ore in 1962. Canadian producers will be at a cost disadvantage competing with South American and African producers for the European markets, but high quality, reliability, and preferential treatment by the British may enable the Canadians to maintain substantial exports eastward. Canada sold 2,850,000 tons of iron ore to European countries in 1962. Canada's capacity to produce high-grade iron ore probably will exceed 60 million tons per year by 1980. Actual output, however, may range substantially below the growth rate indicated by that figure.

Mexico will produce iron ore for its own needs but probably will not export significant quantities. Almost certainly, Mexican iron ore will not affect U.S. markets.

The outlook is for iron ore producers in South America actively to continue supplying ore to the United States, Japan, and European countries. The only readily apparent conditions that could prevent their doing so are political instability and confiscatory taxes. Large, easily mined, high-grade deposits, year-round moderate climate, and in most instances proximity to salt water ports give the South American producers an inherent economic advantage over most other producers.

Transportation probably will continue to be the bottleneck that limits iron ore output in the Minas Gerais district of Brazil. This situation may be alleviated within 5 years by a new rail line from the district to Rio de Janeiro. The outlook is for favorable government action to permit building of such a line. A new line, and enlarged capacity through the part of Vitória will increase Brazil's potential for iron ore exports to 30 million tons per year. Iron ore needs of the Brazilian iron and steel industry will not affect significantly Brazil's capacity to export ore.

Chile's iron ore productive capacity more than likely will remain above its own needs and ability to find markets. Export capacity could reach 20 million tons per year by 1980, but export shipments probably will not increase at a comparable rate.

Peru's iron ore productive capacity is expected to change very little in the next decade or two. Considering the planned developments in Australia and potential developments in the Western United States there is much doubt that there will be incentive for Marcona to install a new plant to obtain more production. Increased efficiency and minor plant additions may increase Peru's export capacity to 10 million tons per year. Output will depend on markets. The Peruvian iron ore industry should be competitive around the world; therefore, an aggressive sales policy could result in exports much higher than the estimated 10 million tons.

The Venezuelan iron ore industry may be on the threshold of a revolutionary technical change that will put it far ahead of its competitors in supplying merchant ore to the world's markets. The government has been asked to approve plans to lay a pipeline from the oilfields of Eastern Venezuela in the State of Anzoategui to the mines in Piar District of Guayana area in the State of Bolivar. The line is to transmit natural gas for use in an iron ore reduction plant to upgrade Guayana ore from 60 to 85 percent iron. The plans call for initial plant annual capacity of 1 million tons of finished product which can be increased readily to 10 million tons.

The natural gas reduction plans greatly enhance the outlook for the Venezuelan iron ore industry. The combination of inexpensive reductant and high-grade, low-silica ore favor a successful operation. An 85 percent iron bearing material with suitable physical properties and stability to stand long-distance transportation would make its own market if offered at prices competitive with the contained iron in pellets and high-grade ore.

Accordingly, it is expected that by 1970 the Venezuelan iron ore industry will have annual capacity to produce 10 million tons of partially reduced ore plus 10 million tons of high-grade ore and that by 1980 the production capacity for partially reduced ore will be increased to 20 million tons.

European iron ore mines, with the exception of those in the Soviet Bloc and on the Scandinavian Peninsula, in the future will not be as significant a source of ore for the European iron and steel industry as they have been in the past. The iron ore industries in Great Britain, West Germany, France, Luxembourg, Spain, Austria, Italy, and Yugoslavia in all probability will either remain static or decline in relation to the size of their cohabitant steel industries.

Iron mines in Sweden, Norway, and Finland do not compare favorably in inherent cost of production with open-pit mines in more temperate and tropical climates. Nevertheless, the iron ore industry of these northern countries will continue to produce on a large scale, although individual small mines may not be able to meet world competition. The outlook is for total mine capacity of 30 million tons annually by 1970 and 40 million tons by 1980.

Among the Soviet Bloc countries only the U.S.S.R. appears to have potential for a growing iron ore industry to serve a market that is demanding higher and higher grade ore. The need of the steel industries of Bulgaria, Czechoslovakia, East Germany, Poland, Hungary, and Rumania for quality raw material to increase output will probably make them part of this market. Thus the outlook for the iron ore industry of the Soviet Bloc is for the mines in U.S.S.R. to expand capacity to supply most of the needs of the Soviet satellites and for many of the low-grade mines of the satellites to close.

It is doubtful that Soviet Bloc ore will move outside the Bloc and probable that free world ore will be shipped into the Bloc. The quantity of free world ore entering the Bloc will be determined by trade agreements similar to those now existing between Brazilian and Indian mining companies and communist governments. Therefore, the iron ore and iron and steel industries in the Soviet Bloc countries will have little if any influence on free world trade in iron ore.

African iron mines are destined to assume a larger role in the iron ore trade of the world. Political stability and economic responsibility probably will be the prime factors influencing the direction of growth. The Liberian industry, judging by past government performances, is the most favorably situated to expand at a rate compatible with potential markets. By 1980 the industry should have capacity to produce 20 million tons per year.

The Mauretanian and Sierra Leone industries have established markets in world trade, and there is no reason to believe that internal circumstances will be altered sufficiently to jeopardize external relations. The industry of Mauretania probably will have iron ore productive capacity of 8 to 10 million tons annually, by 1980. That of Sierra Leone probably will have 3- to 4-million ton capacity.

Gabon has the resources to support a substantial merchant iron ore industry. The extent of development in capacity to produce iron ore will be dependent on the activity in the European steel industry and on government stability. If the government encourages free industrial enterprise through 1970, development of iron ore resources will be dependent on markets for iron ore then existing.

Guinea also has the resources to support substantial merchant iron ore industries, but the apparent course of its government makes it unlikely that private companies will invest the necessary funds.

India is the only Asiatic country expected to increase significantly its capacity to produce iron ore for export. Goa's capacity probably will remain around 6 million tons per year while capacity to produce for export in Malaya and the Philippines will decline. The iron ore industry of India will increase its capacity well in excess of domestic requirements and in addition will maintain capacity to produce 2 to 3 million tons annually more than its export market. The total capacity of the Indian industry is expected to exceed 30 million tons of iron ore per year by 1980.

There is not much doubt that an active, aggressive iron ore export industry will be developed in western Australia by 1970. Its size will be limited only by its competition around the world. Trade agreements with Japan and European countries probably will be instrumental in developing capacity to produce at least 5 million tons per year for export by 1970 which may be increased to 10 million tons per year by 1980. However, if markets can be found for the ore, capacity could reach 20 million tons or more per year by 1970 and 40 million by 1980.

Assuming that super ore carriers are built to minimize the ocean transportation disadvantage in supplying European markets that Australian iron ore producers will have with those on the east coast of South America and the west coast of Africa, Australian capacity to produce iron ore for export should reach 8 million tons by 1970 and 15 million by 1980.

Thus the integrated capacity outlook is that the principal iron mines producing for international trade, excluding those in Communist countries, probably will be able to produce 290 to 300 million tons of high-grade iron ore per year by 1980.

Barring a major war that restricts freedom of the seas, every industrialized nation seems as-

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sured of an adequate supply of high-grade iron ore easily available for a price equal to or less than that now established.

The United States is assured of the iron ore it needs under practically any circumstance as long as the North America transportation system is left intact.

The outlook for the domestic industry has bettered each year since innovation of the taconite industry. This improving situation has been brought about by technologic advance and increasing knowledge. Thus the thesis that the best key to the future is record of the past provides assurance that the domestic industry will fluorish in the next decade with current research and development substantiating this outlook. More than likely producers of high-grade pellets will tend to capture the markets and the producers of partially reduced pellets will take over from them as all the excess blast furnace capacity for smelting standard pellets is utilized. Domestic iron mines are in an excellent position to be in the forefront of this pattern.

Figure 3 shows the U.S. iron ore supply 1940–64 and a forecast of the sources of supply and the rate of consumption 1964 through 1980.

The forecast was made on the basis of anticipated U.S. steel production, which was converted to iron in ore requirements assuming that 0.67 ton of iron from ore would be used to produce each ton of steel. This figure discounts the impact that basic oxygen converters, and continuous casting units could have on the scrap to hot metal ratio. Iron requirements were converted to iron ore assuming an average grade of 60 percent iron for both domestic and foreign ore. U.S. steel production was projected in accordance with the historical use of steel per capita, assuming that it would increase at the 1.6 percent compound annual rate forecast by the Bureau of Mines, for the growth rate of population and labor force. This projection then was modified by consideration of technologic, economic, political, and social elements to forecast an iron and steel industry growth rate slightly above that expected for the U.S. population. The principal elements considered in making the forecast were—(1) better steel, (2) use of substitutes, (3) development of new uses, (4) imports of foreign steel, (5) expansion of foreign markets, (6) less expensive production methods, and (7) shifting U.S. population.

Better quality steel greatly slowed the rate of steel consumption in the last decade, but to the presently produced quality level this factor apparently has exerted maximum influence and therefore will not change the trend significantly in the future.

Use of substitutes and development of new uses for steel have by and large offset one another in the past. Now better quality steel and the steel industry's comprehensive, application research program should begin to bear fruit. New steel uses in the future probably will more than offset use of steel lost to substitutes.

Steel imports probably will exceed exports for the short term (5 years). The determining factor in the balance will be cost and quality. Here again quality and research favor the U.S. industry. Furthermore, the technologic advances and capital improvements of recent years and the probability of continuing advance and improvement put the domestic industry in an increasingly better competitive cost position. This leads to the conclusion that for the long term, steel exports will exceed imports, and the per capita output of steel will tend to increase accordingly.

Changing distribution of people in the United States will tend to cut down per-capita steel consumption because a larger percentage of the people will live outside the Chicago-Pittsburgh industrial complex where steel is the leading structural material.

Reinforced concrete and timber are preferred to steel in the Pacific Coast States, where the population is expected to increase 62 percent between 1960 and 1980, and the Mountain States, where it is expected to increase 55 percent. These increases are in contrast to the total expected population increase of only 37 percent.

These seven elements expected to influence the rate of steel production in large measure offset each other. However, time will tend to strengthen those elements that can increase steel output and weaken those that could decrease it. With this in mind the forecast of a growth rate only slightly higher than rate of population growth is considered conservative.

The forecast of iron ore requirements is a mean from which actual consumption is not expected to vary more than 15 percent, and the total supply—domestic production, plus imports, minus exports—is not expected to vary from actual consumption more than 10 percent. Domestic and Canadian mines producing high-grade iron ore pellets for consumption in the United States are in a position to maintain output near capacity. Those producing lesser quality will necessarily provide most of the flexibility needed to adjust supply to consumption. Iron ore imports from Africa and South American countries are not expected to vary significantly from the quantities shown on figure 3.

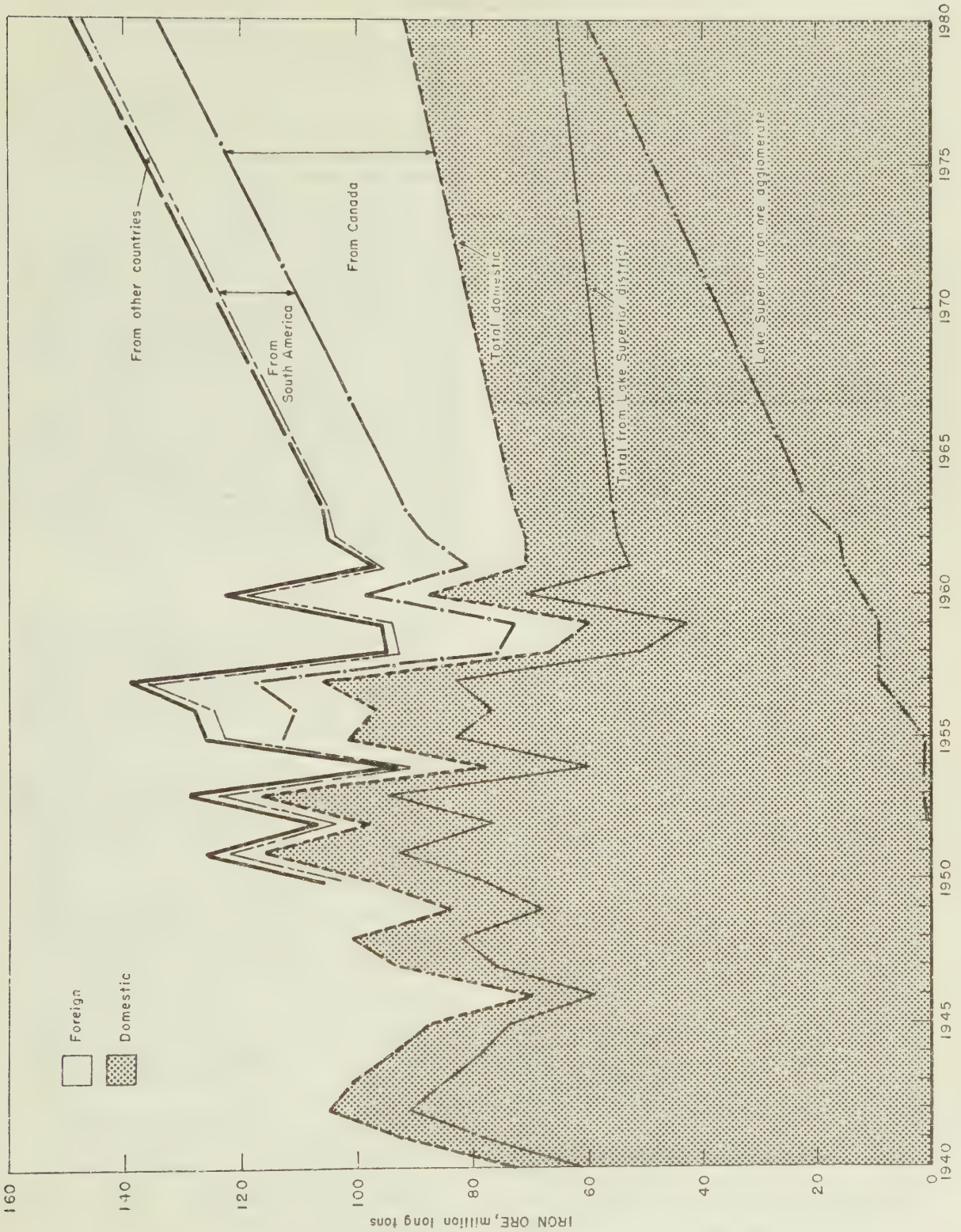

FIGURE 3.—Sources of United States Iron Ore Supply 1940–63 and Predicted Sources 1964–80.

PROBLEMS

The principal problem of the domestic industry is to meet both price and quality competition from foreign producers. It must do so if it is to continue to exist. The domestic industry has proximity in its favor, but all other elements of iron ore production favor one or the other of foreign operations producing iron ore for sale in the United States. This leads to many specific operating problems.

The iron formation in the Lake Superior region is exceptionally hard and fine-grained; consequently, both mining and grinding costs are high. Use of jet piercing equipment for drilling and scientifically designed blasting have been partial solutions to the problem, but the fact remains that mining costs in the Lake Superior district are not competitive with those in Canada.

Loss of the iron minerals not susceptible to magnetic attraction in taconite processing operations in Minnesota and some other districts is a problem. Researchers seem to be approaching an economical solution, but the problem is not yet solved.

More than two-thirds of the iron formation that is equal in grade to that being mined is not profitably amenable to any known method of concentration. Thus, inability to mine and process nonmagnetic taconite is a problem. The same is true of partially oxidized iron formation and soft hematite ores.

Transportation of iron ore is a problem, particularly from the Lake Superior district because there it is a seasonal operation. Not only are transportation costs high, but periodic operation forces consumers to maintain a large iron ore inventory. Agglomeration of fine-grained ore and iron ore concentrate is a solution to smelting these materials but because of the cost, it is not a completely satisfactory solution. Exploitation of titaniferous iron ore deposits is a problem because iron ores containing more than 1 percent of titanium cannot be easily smelted in a blast furnace without excessive operating difficulties and high fuel consumption.

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KYANITE AND RELATED MINERALS

By James D. Cooper [1]

KYANITE and related minerals have been the basic raw materials used in the production of mullite since 1925. Mullite is an important refractory material, and its field of use lies between that of superduty fire-clay refractories and the extra-high alumina refractories. Small quantities of kyanite without calcination also are used in manufacturing glass, electrical and chemical porcelain, pyrometer tubes, and other ceramic products. Kyanite and the related minerals—sillimanite, andalusite, dumortierite, and topaz—all convert to mullite and siliceous glass at from 2,570° to 3,002° F. Mullite is stable and has a low coefficient of expansion up to 3,270° F, making it espécially valuable for refractories subjected to thermal shock. Mullite also may be produced synthetically from mixtures of bauxite, Bayer-process alumina, kaolin, and silica by sintering or fusion.

Until the early 1950's most mullite refractories were made from lump kyanite from India. Wartime circumstances led to greater use of domestic minerals, and postwar supply problems led to greatly increased commercial production of synthetic mullite. There are no known significant domestic sources of lump kyanite or related minerals. There are large domestic disseminated and placer deposits, but the concentrate from these is not as readily usable as the massive type for some applications. Three domestic companies produce concentrate.

The glass and metallurgical industries consume most of the kyanite and mullite produced.

Since mullite refractories are restricted to specialized applications, production is relatively small compared with that of superduty fireclay refractories, which cost substantially less but perform satisfactorily for many uses.

BACKGROUND

SIZE AND ORGANIZATION OF THE INDUSTRY

The domestic mullite industry, including production of kyanite, is relatively small, although its products are highly important for specialized uses. In 1963 about 135 people were employed in mining and milling kyanite, and probably not over 500 people were employed in producing synthetic mullite and manufacturing mullite refractories.

Initially (1917–24), synthesized mullite only was employed. The first synthetic mullite was produced by grinding mixtures of kaolin and alumina and calcining (sintering) at 2,850° F. Also from 1917 to 1924 synthetic mullite was produced by complete fusion of these minerals in the electric furnace.

About 1920 experimentation began with natural minerals. When calcined, the lump material yielded strong large aggregates of mullite crystals whereas the calcined concentrate yielded only fine-grained aggregates. No domestic massive kyanite was known at the time, but small deposits of massive andalusite and dumortierite were found in Nevada and California. Production of these minerals began in 1924 and continued until about 1945. By 1925 massive kyanite from Lapsa Buru in Kharsawan State, India (discovered in 1921) became available, and in 1944 massive kyanite from Kenya also appeared on the market. A topaz deposit near Naples, N.C., was operated from

[1] Commodity specialist.

1940 to 1950, but the material was used mostly as a substitute for fluorspar in steelmaking. Sillimanite production was reported for the first time in Australia in 1932, in India in 1938, and in the Republic of South Africa in 1946.

Concentrate from domestic disseminated kyanite is used as an ingredient in some sintered synthetic mullites, in ramming and mortar mixes, as the fine fraction in mullite brick and shapes, and in many ceramic products. In 1963 the kyanite producers were—Kyanite Mining Corp. at Baker and Willis Mountains, Va.; Commercialores, Inc., at Henry Knob, near Clover, S.C.; and Aluminum Sillicates, Inc., at Graves Mountain, near Washington, Ga.

The following firms produced synthetic mullite in 1963:

Firm and location	*Plant location*
The Babock & Wilcox Co., Refractories Division, New York, N.Y.	Augusta, Ga.
The Carborundum Co., Niagara Falls, N.Y.	Niagara Falls, N.Y.
Harbison-Walker Refractories Co., Pittsburgh, Pa.	Eufaula, Ala.
Norton Co., Worcester, Mass.	Huntsville, Ala.
H. K. Porter Co., Inc., Refractories Division, Pittsburgh, Pa.	Shelton, Conn.
Remmey Division of A. P. Green Fire Brick Co., Philadelphia, Pa.	Philadelphia, Pa.
The Chas. Taylor Sons Co., subsidiary of National Lead Co., Cincinnati, Ohio	South Shore, Ky.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

The kyanite and related minerals group of aluminum silicate minerals is comprised of kyanite, sillimanite, andalusite, dumortierite, topaz, and mullite. Kyanite, sillimanite, and andalusite have the same chemical formula but differ in crystal structure. Dumortierite contains some boron, and topaz is an aluminum fluosilicate. Mullite is obtained commercially by conversion of kyanite and related minerals at high temperatures. Synthetic mullite is made by sintering or fusing bauxite or alumina combined with kaolin or silica. Commercial specifications are lacking for the kyanite minerals and synthetic mullite. Consumers select material on the basis of chemical analyses, grain structure, and strength, and by determination of the Pyrometric Cone Equivalent (P.C.E.) usually by the method specified in ASTM Designation C–24.

National Stockpile Material Specification P–27, as revised in 1960, covers Indian lump kyanite and high-purity electrically fused synthetic mullite (*12*).[2]

[2] Italicized numbers in parentheses refer to the items in the list of references at the end of this chapter.

Although mullite refractories in general serve a temperature range higher than that of superduty fire-clay refractories and lower than that of alumina refractories, there is no sharp demarcation between classes of refractories. In addition, properties such as spalling characteristics, load-bearing capacity, and coefficient of expansion influence the selection of a specific refractory for a specific duty. Final selection is based on use-cost considerations, often without adequate data.

TECHNOLOGY

Geology and Mineralogy

Kyanite and related minerals are of metamorphic origin, and deposits of these minerals are restricted largely to highly metamorphosed areas, although some transportation away from the immediate area may occur. Because of their hardness and chemical stability, kyanite mineral deposits often form low ridges and hills. Most of the deposits of economic value are masses of kyanite or related minerals in quartzites, quartz and quartzite muscovite schists, or as residual boulders of kyanite rock and kyanite-quartz schist. Kyanite and sillimanite also occur in the heavy mineral fraction of beach sands.

Kyanite is an aluminum silicate which in the pure form has the formula $Al_2O_3 \cdot SiO_2$. Related minerals are sillimanite ($Al_2O_3 \cdot SiO_2$), andalusite ($Al_2O_3 \cdot SiO_2$), dumortierite ($8Al_2O_3 \cdot B_2O_3 \cdot 6SiO_2 \cdot H_2O$), and topaz ($Al(F \cdot OH)_2AlSiO_4$). All these minerals have the property, when heated to the proper temperatures, of transforming to mullite $3Al_2O_3 \cdot 2SiO_2$ plus SiO_2. For example, with kyanite, conversion begins at approximately 2,012° F and is completed at about 2,700° F (*12*). The mineral mullite rarely occurs in nature.

Mining

Deposits of massive kyanite and sillimanite, are largely on or near the surface and require hand mining only. Domestic disseminated kyanite deposits are mined by open-pit methods. Blasting is required and power shovels are used for loading. Beach sands are mined using power shovels or dragline excavators.

Milling and Heat Treatment

Massive kyanite is crushed and screened and ordinarily is converted to mullite by heat treatment before use in refractories. Sillimanite often is used in refractories without first being converted to mullite. Domestic kyanite ores are crushed, ground, and processed by flotation,

magnetic separation, and other means to produce kyanite concentrates suitable for use in refractory and ceramic products. The primary gangue minerals are quartz and mica, and the lesser impurities consist mostly of pyrite, iron oxides, and rutile (*9*, *15*).

When undergoing heat treatment, kyanite expands substantially, and for this reason it is precalcined for many uses. The expansion is an asset in some applications, such as mortars or where the expansion offsets the shrinkage of the bonding clay. All of the other kyanite group minerals expand very slightly under heat treatment but not enough to require precalcination. The boron in dumortierite and the fluorine in topaz volatilize during calcination. Sillimanite may be processed in the same manner as massive kyanite, but beginning about 1954, in England and Germany, some Indian sillimanite has been cut into blocks and shapes and used directly in furnace linings. A complete stack lining of sillimanite was installed in a steel blast furnace in England in 1959. The expansion during conversion to mullite is so slight that conversion under working conditions is accomplished without noticeable change.

A special problem in converting topaz to mullite during calcination is the safe disposal of the fluorine gas evolved. There are several processes that could accomplish this, one of which was tried on a pilot-plant basis by the Tennessee Valley Authority using topaz from the Brewer mine. The mullite was of good quality, but the calcium fluoride produced was of doubtful value as a salable byproduct (*14*). The cost of a degassing plant using any of the processes, however, would be too great for the tonnage of topaz in the Brewer mine.

Manufacture of Synthetic Mullite

Fused mullite is prepared in electric furnaces, and the materials used are the purest quality obtainable. Bayer-process alumina, produced principally from the Caribbean and South American bauxite, and high-purity silica sand are the principal ingredients. The final product is superior to that made from the best massive Indian kyanite. It is more costly, but is necessary for some special uses.

The raw materials for both types of sintered mullite are mixed thoroughly by ball-mill grinding, screened, pugged with water, and extruded in a column. The column is cut into lengths called slugs or dobies which are then sintered to produce mullite. The sintered material, or "grog", is crushed, ground, passed over a magnetic separator, and screened. To produce refractory brick and shapes, the grog is bonded and formed by power pressing, and the products fired.

Much of the high-temperature sintered mullite is made from materials comparable to those used for making fused mullite. The sintering is done at about 3,200° F. The product is at least equivalent to that obtained from the best grade of massive Indian kyanite and is perhaps somewhat less costly.

Low-temperature sintered mullite usually is made with a good grade of low-iron (about 2.75 percent Fe_2O_3 maximum) siliceous bauxite as the chief raw material. The sintering is done at approximately 2,800° F, thereby substantially reducing the processing cost compared with the high-temperature sintering method. Data that are available indicate that the quality of low-temperature sintered mullite is approximately equal to that produced from Indian kyanite.

USES

The manufacture of mullite refractories accounts for most of the kyanite and related minerals consumed annually, but nonrefractory uses are expanding.

Most mullite refractories are used as furnace linings in metallurgical and glass manufacturing furnaces. The remainder is used largely for kilns, kiln furniture, and saggers by the ceramic industry and in boilers. Small quantities of kyanite without calcination are used as a source of alumina in the manufacture of glass, electrical and chemical porcelain, pyrometer tubes, and in the form of kyanite concentrate to increase the alumina content of fireclays. Kyanite is used to improve workability, increase strength, and to compensate for firing shrinkage in floor and wall tile and other ceramic products.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

In Florida beach sand deposits mined for ilmenite, rutile, and zircon, the heavy fraction of tailings from milling operations consist principally of kyanite, sillimanite, and staurolite. Bureau of Mines research at the Tuscaloosa Metallurgy Research Center, Tuscaloosa, Ala., developed a method for producing a concentrate averaging 90 to 95 percent of a mixture of kyanite and sillimanite, with a recovery of 70 to 75 percent (*2*).

ALTERNATE MATERIALS

Specific substitutes for kyanite and related minerals are two types of synthetic mullite, fused and sintered. Bauxite, or alumina derived from bauxite is the principal raw material for synthetic mullite production. Secondary materials that may be used are kaolin and other clays, silica, and kyanite concentrate. For-

mulas and many processing details are trade secrets.

Alternates consist for the most part of superduty fireclay, high alumina, and pure alumina refractories. None of the alternate materials are entirely satisfactory from all standpoints, including initial cost, ultimate cost, service life, production rates, and quality of finished products.

RESERVES

Reserves of disseminated kyanite group minerals in the United States are large, but data are incomplete. Deposits presently exploited in three districts in the Eastern States contain a measured and indicated reserve of about 100 million tons of quartzose rock with 10 to 30 percent kyanite. These are—Farmville district, Va., 50 million tons; Kings Mountain district, N.C. and S.C., 40 million tons; and Graves Mountain, Ga., 10 million tons (*5*, *12*). Other deposits of kyanite-group minerals in quartzose rocks occur in the Eastern States and in California, Nevada, and New Mexico. Reserve data are lacking for all except the Petaca district, N. Mex., which contains an estimated reserve of 2 million tons of medium-grade ore (*5*).

Many hundred million tons of kyanite-bearing schists and gneisses containing about 10 percent kyanite are present in the Burnsville-Swannanoa belt of North Carolina. Large quantities of similar but somewhat lower grade material are present in Habersham and Rabun Counties, Ga. (*5*).

The Boehls Butte quadrangle in Idaho has large deposits of gneisses and schists which contain kyanite, sillimanite and andalusite that may have potential value. Bureau investigations in Idaho indicate that there are many tens of millions of tons of kyanite garnet schist containing 15 to 45 percent kyanite in the Woodrat Mountain area, and a like quantity of kyanite schist and gneiss of lower grade in the Goat Mountain area. An outcrop of kyanite schist with an estimated thickness of more than 50 feet and containing about 10 percent kyanite has been found in the Albion Range in Cassia County.

Other deposits of kyanite group minerals in metamorphosed argillaceous rocks occur in New York, Wisconsin, New Hampshire, Maine, and Massachusetts.

Titaniferous beach sands in Florida contain kyanite and sillimanite in addition to other heavy minerals. Although recovery of the kyanite group minerals is not considered economic at present, a reserve of about 12 million tons of contained kyanite is available for future use (*12*).

The only known reserve of massive kyanite in the United States is a 5,000-ton deposit at Willis Mountain, Va. (*12*).

The deposits of massive kyanite in India are the best known foreign deposits, having been worked since the 1920's. The kyanite belt in Singhbhum district, Bihar State, is 70 miles long, with local enrichments. The largest deposit is at Lapsa Buru at the western end of the belt. Recent reserve estimates are lacking, but production at Lapsa Buru has far exceeded a 1929 estimate of about 214,000 tons of surface boulder material, and production has increased in recent years. A later estimate indicated that there is about 750,000 tons of kyanite to a depth of 10 feet. The sillimanite deposits in the Kasia hills, Assam, contain about 2 million tons according to a recent estimate, which presumably includes deposits of disseminated mineral. Other significant deposits of kyanite group minerals occur in Mysore and Travancore.

The reserve of andalusite-quartzite at Semiz Bugu, Kazakh S.S.R. is estimated to be 72 million tons of rock containing 18 percent andalusite. Approxiately 50,000 tons of andalusite occurs in a placer deposit at Chaingt, eastern Siberia.

The known reserves in European U.S.S.R. occur on the Kola Peninsula. At Kiev, reserves of 54 percent andalusite ore in metamorphosed sediments total 3.6 million tons, and at Lovozero an andalusite-nepheline syenite deposit contains 200,000 tons of ore with 30 percent andalusite.

A reserve of several million tons of kyanite is reportedly available in the Wipp Valley of the Tyrol, Austria. In Bulgaria a deposit containing about 900,000 tons of kyanite was reported in the Rhodope Mountains.

At Boliden, Sweden, andalusite occurs in irregular bodies in altered volcanic rocks. The bodies are up to 35 meters thick and 170 meters long.

Kyanite group minerals occur in economic quantities in North Korea and South Korea. At Pyonggang-gun, Kangwon-do, North Korea, a kyanite deposit with 200,000 tons was known prior to the Korean conflict. There is a large deposit of kyanite-biotite-schist at Kangso-gun, P'yongan Namdo, North Korea. In South Korea actively mined deposits are at Ch'ongwon' gun Ch'ungch'ong-Bukdo and Sosan'gun Ch' ungchi'ong-Namdo. No reserve data are available. A large deposit of sillimanite schist containing 10 to 30 percent sillimanite was recently reported at Nonsangum, Ch'ung Ch'ong Namdo about 200 miles south of Seoul, and attempts to beneficiate the ore were underway in 1964.

Reserves of massive kyanite in the Murka-Loosoito belt in the Taveta district in Kenya

have been substantially depleted as has the reserve of massive sillimanite in the Pella area in Cape Province, Republic of South Africa. Large reserves of disseminated kyanite and sillimanite are still available. Deposits of andalusite in river sands in the Marico district, western Transvaal, Republic of South Africa are estimated to contain at least 400,000 tons of recoverable andalusite. A deposit containing 20 to 30 percent andalusite has recently been explored in northern Transvaal southeast of Pietersburg. The deposit is about 300 feet thick and at least 15 miles long. Elsewhere in Africa deposits are in Angola, Cameroon, Swaziland, and Malawai (formerly Nyasaland).

Kyanite group minerals occur in Australia, but known reserves are not large. Reserves of sillimanite at Broken Hill, New South Wales and Mt. Crawford, South Australia, where most of the production has been reported are probably less than 25,000 tons. Other deposits or occurrences of kyanite group minerals are in the Olary district, South Australia, and in Youmah and the Chittering Valley, Western Australia.

SOURCES OF STATISTICAL INFORMATION

Domestic production of kyanite and synthetic mullite is reported annually to the Bureau by domestic producers. Foreign production data are obtained by the Department of State and published by the Bureau of Mines. Import and export data are compiled by the Bureau of the Census and published annually by the Department of Commerce.

PRODUCTION, CONSUMPTION, AND TRADE

World production of kyanite and domestic production of synthetic mullite are shown in table 1.

Figures on domestic production of kyanite and consumption of kyanite and mullite are withheld by the Bureau to prevent disclosing individual company confidential data.

Imports and exports of kyanite and related minerals are shown in table 2.

TABLE 1.—*World production of kyanite and related minerals, 1928–63*

[Short tons]

Year	United States		Africa					India		Republic of Korea, andalusite [1]	Australia, sillimanite [2]
	Kyanite and sillimanite	Synthetic mullite	Bechuanaland, kyanite	Southern Rhodesia and Nyasaland, kyanite	Kenya, kyanite	South-West Africa, kyanite and sillimanite	Republic of South Africa, andalusite and sillimanite	Kyanite	Sillimanite		
1928	(3)							2,510			
1929	(3)							4,052			
1930	(3)							9,678			
1931	(3)							3,821			
1932	(3)							6,250			34
1933	(3)							4,797			146
1934	(3)							10,540			179
1935	(3)							22,291			17
1936	(3)							27,761	155		34
1937	(3)							30,168			56
1938	(3)							31,791	183		22
1939	2,950							11,106			84
1940	4,241							9,542	248		278
1941	8,335							14,078	228		1,072
1942	8,708							17,154	263		1,727
1943	9,561							14,015	273		1,222
1944	(4)				685			14,671	46		874
1945	(4)				178			15,117	34		1,025
1946	(4)				2,947		6,056	15,108	74		1,001
1947	(4)				16,215		11,546	16,073	264		3,786
1948	14,552				16,352		3,793	14,118	239		2,040
1949	12,115				26,054		4,622	22,343	1,091		1,376
1950	(4)	5 8,000			11,922		8,320	39,747	1,652		1,771
1951	(4)	5 21,000	2,222		11,917	65	12,663	47,501	4,534		976
1952	(4)	5 14,000	2,385	45	9,448	3,000	21,477	30,108	5,685		1,493
1953	(4)	5 18,000	1,960	1,353	6,086	2,717	11,772	17,219	6,150	802	3,984
1954	(4)	5 14,000	2,054	1,624	4,500	140	18,174	47,410	3,434	2	2,617
1955	(4)	5 17,000	840		3,031	240	19,359	13,150	2,714		3,000
1956	(4)	5 24,000	981			2,196	30,244	22,551	5,193		2,443
1957	(4)	19,873	120			3,890	49,509	26,324	8,307		2,578
1958	(4)	16,280			600	2,985	34,490	28,689	15,506	1,218	1,900
1959	(4)	18,218			1,629	3,243	49,591	18,187	8,483	2,438	4,069
1960	(4)	21,497			1,417	1,438	69,137	22,218	9,083	270	1,707
1961	(4)	14,798				3,000	102,301	29,933	8,943	562	2,001
1962	(4)	19,021				1,667	79,367	54,693	9,100	504	2,953
1963	(4)	29,588		60			73,027	34,904	12,439	2,208	3,937

[1] Includes 1,450 tons of kyanite in 1963.
[2] Includes kyanite production as follows: 22 tons in 1938; 157 tons in 1946; 3,283 tons in 1947; and 1,260 tons in 1948.
[3] Data not available.
[4] Data withheld to prevent disclosing individual company confidential data.
[5] Estimate.

TABLE 2.—*U.S. imports for consumption and exports of kyanite and related minerals*

Year and country	Short tons	Value
Imports:		
1954–58 (average)	5,464	[1] $240,129
1959	5,633	251,638
1960	6,052	265,364
1961	5,415	244,189
1962:		
North America: Canada	108	9,980
Asia: India	3,845	174,948
Africa: South Africa, Republic of	1,328	49,483
Total	5,281	234,411
1963:		
North America: Canada	59	5,287
Asia: India	2,500	110,532
Africa: South Africa, Republic of	65	3,299
Total	2,624	119,118
Exports:		
1954–58 (average)	1,855	93,057
1959	2,734	167,432
1960	3,255	209,950
1961	4,000	317,633
1962:		
North America:		
Canada	611	100,480
Dominican Republic	2	208
Mexico	587	33,073
South America:		
Argentina	53	3,028
Colombia	15	757
Venezuela	81	3,782
Europe:		
Belgium-Luxembourg	30	1,377
Finland	30	1,746
France	99	7,012
Germany, West	719	45,464
Italy	424	28,426
Portugal	3	384
Sweden	20	1,020
United Kingdom	530	30,754
Yugoslavia	22	5,452
Asia:		
Hong Kong	4	1,000
Indonesia	57	3,248
Japan	242	15,792
Oceania: Australia	39	3,737
Total	3,568	286,740
1963:		
North America:		
Canada	765	133,360
Mexico	698	42,952
Trinidad and Tobago	6	1,156
South America:		
Argentina	44	2,500
Brazil	2	586
Uruguay	3	667
Venezuela	228	16,409
Europe:		
Finland	40	2,304
France	204	38,669
Germany, West	939	53,524
Italy	459	42,535
Netherlands	18	1,007
Spain	53	5,491
United Kingdom	625	40,782
Asia: Japan	862	53,203
Africa: Sudan	1	252
Oceania: Australia	103	6,673
Total	5,050	442,070

[1] 1954 data known to be not comparable with other years.

Source: Bureau of the Census.

The only tariff effective in December 1963 on kyanite and related minerals was 15 percent ad valorem for calcined kyanite. There was no tariff on crude material.

STRATEGIC CONSIDERATIONS

Only Indian lump kyanite and electrically fused synthetic mullite are presently classified as strategic. In an emergency a conversion from use of Indian kyanite to synthetic mullite could be made in a relatively short time, but a few thousand tons of the Indian material is retained in the national stockpile to provide for the transition period. Production of the highest purity fused synthetic mullite is not great, and industry does not maintain large stocks. Large quantities of electrical power are required for its production, and in an emergency the power requirements for other important uses would increase. Therefore, a modest quantity of high-purity electrically fused mullite is included in the national stockpile. On June 30, 1964, inventories totaled 8,645 tons.

Production capacity for all types of synthetic mullite and domestic kyanite concentrate are adequate to supply emergency requirements. Small quantities of Bayer-process alumina would be required for the highest quality synthetic mullite. Domestic low-iron siliceous bauxite, with or without addition of domestic kyanite concentrates, could be used for all of the less exacting qualities of synthetic mullite.

GOVERNMENT PROGRAMS

Kyanite is on the list of minerals eligible for exploration assistance from the Office of Minerals Exploration, Department of the Interior. Under this program the Government will advance 50 percent of approved costs of exploration programs for kyanite.

PRICES AND COSTS

Kyanite prices as of December 1963 were as follows: Per ton, f.o.b. point of shipment, Virginia and South Carolina, 35-mesh, carload lots, in bulk, $44 to $45, in bags, $47; 200-mesh, in bags, carload lots, $53 to $55; imported, 60-percent grade, in bags, c.i.f. Atlantic ports, $76 to $81 per short ton.

Synthetic mullite prices are not quoted on the open markets as are those of kyanite but are subject to quotation from individual producers. The prices depend upon the type of manufacture, degree of processing, and specifications required by the individual consumer. In 1963 the average value of the mullite produced as reported to the Bureau was $120 per short ton. Special products are valued at several hundred dollars per ton.

TAXES

There are no special taxes imposed on the kyanite industry. Producers are granted a depletion allowance of 23 percent on domestic production and 15 percent on foreign production.

RESEARCH

Research on mulite was started by the National Bureau of Standards in 1917 (*12*).

Since 1924 the Bureau of Mines has conducted research intermittently on kyanite and related minerals (*16*, *17*, *19*, *22*). The effects of major impurities on the properties of mulite and the possible uses of the Florida beach sand tailings were investigated (*2*). Substantial research was done on the concentration of ores from Georgia and South Carolina sillimanite deposits (*10*) and later on Florida beach sand tailings (*23*). The Bureau investigated and reported on several occurrences of kyanite, sillimanite and topaz in the southeastern States (*10*, *11*, *15*, *18*) and presently is investigating occurrences of kyanite and related minerals in the Pacific Northwest.

The development of the technology of fused and sintered synthetic mullite is done almost wholly within the refractories industry. Very little research has been published.

OUTLOOK

The outlook for domestic consumers of kyanite, sillimanite, andalusite, and synthetic mullite has improved greatly during the past decade so that at present the United States is essentially independent of Indian and African sources of mullite-forming raw materials.

Synthetic mullite made from readily available raw materials now accounts for more than 80 percent of the strategic mullite used in the United States. This percentage should remain fairly stable during the next 5 years while the total domestic requirement for strategic mullite will probably increase about 5 percent per year. Production capacity for both sintered and electrically fused synthetic mullite is substantially in excess of actual production, and additional capacity is planned by some producers. Manufacturing processes for sintered synthetic mullite have been improved, and additional improvements are expected as research on mullite structure advances.

Until the early 1950's imported kyanite accounted for practically all of the strategic mullite used in the United States. In recent years imports amounted to only about 20 percent. Although imports should continue to supply a small part of the Nation's requirements, in an emergency synthetic mullite production could be increased easily to compensate for any reduction of imports.

Total free-world requirements for kyanite group minerals and mullite are increasing about 5 percent per year. This rate should be accelerated during the next 5 years by industrial expansion in underdeveloped countries, particularly India. Reserves and production facilities are adequate to meet the requirements.

There has never been a shortage of minus 35-mesh domestic kyanite concentrates which are used in mortar and ramming mixes, as the fine fraction in mullite brick and shapes, as an additive to increase the alumina content of fire clays, and in ceramic body mixes. The use of domestic kyanite will probably increase 8 to 10 percent per year until 1970.

New uses for mullite refractories have been proposed, and if adopted they could increase mullite requirements at a faster rate. The major potential new application proposed is for lining blast-furnace stove sections and other critical sections of blast furnaces. Metal-fiber-reinforced mullite has been successfully tested for use on the leading edges of wings for hypersonic aircraft.

PROBLEMS

The principal problem regarding mullite refractories is regional shortages of mullite-forming raw materials. In the Western States, mullite refractories or the raw materials used to produce them, are now shipped in. This increases the cost to such an extent that mullite refractories cannot be used for many of the purposes for which they are suited. Mullite-forming raw materials, if available locally at reasonable cost, could also be used to increase the refractoriness of low-grade or subgrade fire clays.

Another problem concerns the availability of domestic bauxite for use in manufacture of low-temperature sintered synthetic mullite. The best material for this use is siliceous bauxite containing not more than 5 parts per hundred of the combined impurities Fe_2O_3, TiO_2 and alkalies, of which a maximum of 2 parts per hundred can be alkalies (*22*). Short-term require-

ments can be met from known domestic reserves, but additional reserves need to be found for long-term requirements.

An important problem of long standing concerns the lack of adequate specifications for kyanite minerals and mullite. The only current published specification is the Government's stockpile Specification P–27–R, which covers Indian lump kyanite and fused synthetic mullite (*12*). Specifications are needed for the domestic kyanite-group minerals and the minerals used to make sintered synthetic mullite to enable proper appraisal of the numerous deposits which are not presently being exploited.

Testing methods are presently inadequate and are cumbersome, difficult, and time-consuming. Many commercial ceramic testing laboratories are not equipped to conduct complete evaluation tests for kyanite and mullite. Fast, simplified, low-cost testing methods are needed by refractories manufacturers and by Government and commercial testing laboratories.

There are no published use-cost comparison studies between mullite refractories and other refractories used in the same temperature range. Such studies would be valuable in promoting more efficient use of refractory raw material resources.

Economical beneficiation methods are needed for kyanite-group minerals in the Western States.

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LEAD

By Donald E. Moulds [1]

LEAD was one of the earliest metals utilized by man because of ease of refining and fabrication and widespread occurrence in areas of ancient civilization. Man still utilizes lead for corrosion-resistant sheets, piping, and many other ancient applications, and, in addition, a host of new uses have been developed to maintain its position as a leading industrial metal.

Lead ore is produced in over 50 countries and refined in 37 countries. World trade in lead ores and metal is a significant factor in the economics of several countries having ore-producing and/or metal-refining capacity surplus to domestic needs for lead and are thus exporters to lead-deficient industrial nations. World production of lead was 2.8 million tons in 1963. Australia leads in mine production followed by the U.S.S.R., United States, Mexico, Canada, and Peru. The United States is the leading producer of metal followed by the U.S.S.R., Australia, Mexico, Canada, and West Germany. The leading consumers of lead, in order of importance, are the United States, U.S.S.R., West Germany, United Kingdom, France, and Japan.

U.S. mine production in 1963 was about 253,000 tons, or 9 percent of world production. Mine production supplemented by imports of concentrates and bullion provided a domestic refinery output of 395,000 tons, approximately 14 percent of world primary refined metal. Primary production further supplemented with secondary lead and imported metal supplied the U.S. requirements of 1.16 million tons of lead in 1963.

Demand for lead increased substantially in 1962–63, and a continuation of the upward trend is indicated to meet the rising industrial consumption, especially in the field of transportation. Research and development in the industrial field have resulted in new applications as well as improvements in techniques and products for the historical applications and have maintained lead's competitive position.

World reserve of lead in ore, currently estimated at 50 million tons, is being added to at a rate in excess of depletion by mining operations. New developments, notably in south-central Missouri and in Canada, promise major additions to reserves and production potential in the near future. The strategic position of lead in the United States is excellent in view of the domestic productive potential, large government inventories, and availability of lead from neighboring Mexico and Canada. The current outlook is for a short-term, through 1966, supply deficit until presently planned mine and smelter facilities provide the domestic production potential necessary to meet the long-term requirements.

The major problem of the lead industry is to maintain a supply of ore and metal in coordination with expanding world demand at prices that encourage growth in use of the metal. This problem has many facets—mineralogical, industrial, geographical, and geopolitical. The lead industry needs to expand in coverage, and detail world statistics on which to base industry appraisal of the total situation with relation to mine production smelter output and world requirements to alleviate imbalances and resulting market disruption.

BACKGROUND

Lead's uses in pipe, sheet metal, weights and solders, and as an ingredient in glass and ceramic glazes were known in various degrees by the ancient Egyptians, Phoenicians, Greeks, and Romans. The Phoenicians worked lead mines in Cyprus, Sardinia, and Spain. The famed lead-silver mines of Laurium, Greece, supplied the ancient Greeks with much revenue. The great quantities of silver that enriched Rome for

[1] Commodity specialist.

six centuries were derived from lead smelting-refining operations in Spain, Sardinia, and Britain.

Lead was mined and smelted in Virginia as early as 1621, and the discovery of lead in the Upper Mississippi Valley was reported in 1690. Various efforts were made by the French to establish lead-mining operations in what is now the southeast Missouri lead district, during the first part of the 18th century, but production was negligible. The shallow mines of the Upper Mississippi Valley were important sources of lead during much of the 19th century. In 1867, discoveries in southeast Missouri at depths of over 100 feet led to development there of one of the two most productive lead regions in the world. The year 1961 marked the 54th consecutive year in which southeastern Missouri was the leading lead-producing mining district in the United States; the lead was lost to Idaho in 1962 because of a long strike at the St. Joseph Lead Co.

Lead production in the United States was annually about 1,000 tons from 1801 through 1810 but increased progressively to about 13,000 tons of lead a year from 1831 to 1840, approximately 10 percent of world output. Missouri and Upper Mississippi Valley areas were the principal producing regions. Lead production from 1840 through 1870 was essentially at the same rate as in 1831–1840.

Completion of the first transcontinental railway in 1869 gave further impetus to the lead-mining industry. An era of prospecting followed that led to discovery and development of lead deposits at Eureka, Nev.; Bingham Canyon, Park City, and Big and Little Cottonwood Canyons, Utah; Leadville, Colo.; Cerro Gordo, Calif.; Bonne Terre and Joplin, Mo.; and in the Coeur d'Alene region, Idaho. Production increased sharply in the 1870's, and both mine and smelter production grew rapidly during the 1880's and 1890's. The United States became the world's largest lead producer in 1893, and for 1891–1900 production annually exceeded 200,000 tons, or more than 25 percent of the total world output. Production increased remarkably from 1900 through 1929. In 1900, mine production of recoverable lead totaled 270,000 tons, and by 1925 it was 684,000 tons—more than one-third of total world output.

The stock of refined and antimonial lead at primary plants continued to increase, as consumption of lead declined reaching 207,200 tons at the end of January 1962. Industrial activity in the United States resumed an upward trend in early 1962 and lead consumption has shown a substantial increase beginning in January 1962. A strike at the Missouri Mines of St. Joseph Lead Co. which began on July 27, 1962, and terminated on April 1, 1963, along with quota restricted imports necessitated a heavy drawdown of producer stocks to meet the increasing domestic requirements and by the end of June 1964, primary producer stocks had been reduced to 29,000 tons and consumers were experiencing difficulty in obtaining sufficient metal. Outside the United States, production and demand were essentially in balance in mid-1964, in contrast to the surplus existing in prior years.

Many new techniques to improve mining, milling, and smelting were introduced or gained wide acceptance in this period. These techniques included mechanized haulage underground, use of centrifugal pumps, wide spread use of froth flotation (including differential flotation) and the development of sintering devices to improve the structure and smelting qualities of the blast furnace feed. In 1919 recovery from scrap first exceeded 100,000 tons and became the important element of lead supply that it still is, comprising over a third of the U.S. total lead supply.

The United States has continued to be one of the world's leading lead-mining nations since 1929; but owing to increased requirements, beginning in 1939, imports of ores and metal have been required to augment domestic mine production and secondary metal recovery to meet the expanding needs of domestic industry.

The decades following 1940 were marked by fluctuating production and consumption resulting from World War II, post-war recession, Korean hostilities, and the following recession. Expanded world production necessitated by war demands was surplus to a peacetime economy, and thus the supply-demand balance was in continual flux. The U.S. market was especially attractive to surplus foreign production after the Korean war, and excessive imports in comparison to reduced consumption resulted in an unprecedented tonnage of lead in U.S.-producer stocks. In late 1958, the United States invoked import quotas on foreign lead ore and metal to reduce these stocks (*16*).[2]

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Lead ranked fifth in tonnage of metals produced in the world in 1963, following steel, aluminum, copper, and zinc in that order. The United States was the world's foremost producer of lead as ore and as refined metal from 1893 through 1956. In 1957, Australia gained first place in mine production, and in 1958,

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

Australia and U.S.S.R. both surpassed the United States; the estimated refined metal production of U.S.S.R. exceeded primary production of the United States in 1959 and again in 1962. The countries of the Western Hemisphere produced 32 percent of the 1963 mine output of the world.

There are approximately 90 primary smelters and refineries in 29 countries ranging in annual capacity from less than 1,000 tons to the 246,000 tons of the Port Pirie, Australia, smelter of Broken Hill Associated Smelters Pty., Ltd. The refined lead output of the principle six countries, United States, U.S.S.R., Australia, Mexico, West Germany, and Canada, was 60 percent of the world output, and that of the Western Hemisphere about 33 percent.

The U.S. primary lead industry is composed of about 500 companies engaged in mining, smelting and refining, and marketing lead. In mining, seven companies—the St. Joseph Lead Co., United States Smelting, Refining & Mining Co., the Bunker Hill Co., American Smelting & Refining Co., the Eagle-Picher Co., The Anaconda Company, and National Lead Co.—produce more than 65 percent of the domestic output. The first 6 of these companies own the 10 primary lead smelters and refineries in the United States, and the National Lead Co., with American Smelting & Refining Co., operates secondary smelters having almost 50 percent of the total U.S. secondary capacity. The same seven firms together with American Metal Climax, Inc., and C. Tennant Sons & Co. (sales agents for important foreign producers) are leaders in competitive lead marketing, and all the companies, except United States Smelting, Refining & Mining Co., the Bunker Hill Co., The Anaconda Company, and C. Tennant Sons & Co., have lead mines abroad.

The secondary lead industry constitutes an integral part of the lead industry. Scrap lead is processed at both primary and secondary smelting plants to yield refined lead, antimonial lead and various lead alloys. In all, about 200 companies melt and smelt lead scrap, and the total lead recovered from scrap materials has exceeded domestic mine production since 1945 and in many years has exceeded production of primary refined lead from both domestic and imported ores.

About 96 percent of domestic mine lead output is from the area west of the Mississippi River. Nearly 60 percent of the lead mine production of the United States since 1875 has been from the Western States, chiefly Idaho, Utah, Colorado, Montana, Washington, Arizona, and California. The most important western districts or regions are the Coeur d'Alene, Idaho; West Mountain, Utah; Summit Valley (Butte), Mont.; Metaline, Wash.; and Upper San Miguel, Colo.

The remaining mine production comes predominantly from the West Central States with minor amounts from the Eastern States. The southeastern Missouri lead district has been the leading producer of lead in the United States since 1909 except for 1962 when production was curtailed by a strike. Geographic distribution of the lead industry on a world basis is shown in detail in the world lead production tables 12 and 13.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Lead is a metal element, chemical symbol Pb; group IV and series 9 of the periodic system; atomic number 82; chemical atomic weight 207.21; stable isotopes 204, 206, 207, and 208; and radioactive isotopes 209, 210, 211, and 214. It is a soft, heavy metal, malleable but only slightly ductile. The specific gravity is 11.35 for cast lead at 20° C. The melting point is 327.4° C and the boiling point about 1,700° C at 760 millimeters pressure. Lead is the ultimate decomposition product of certain radioactive disintegrations; that from uranium has an atomic weight of about 206; that from thorium, 208.

Refined lead is marketed for use in the following seven grades: Corroding, chemical, acid, copper lead, common desilverized A, common desilverized B, and soft undesilverized. Specifications for these are given in table 1.

Large quantities of lead are marketed in various lead- and copper-base alloys. The lead-base alloys are roughly classified into bearing alloys, solders, type metals, low melting alloys, and the numerous antimony or hard lead alloys. The copper-base alloys containing lead are various grades of leaded brasses and leaded bronzes.

Secondary lead is lead derived from salvage of wornout end-product items, such as battery plates, cable covering, pipe and sheet, which are collected, remelted, and refined in secondary smelters to produce refined lead or various lead-base alloys.

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TABLE 1.—*Chemical specifications for commercial pig lead*

	Corroding lead [1]	Chemical lead [2]	Acid lead [3]	Copper lead [4]	Common desilverized lead A [5]	Common desilverized lead B [5]	Soft undesilverized lead [6]
Silver—maximum percent	0. 0015	0. 020	0. 002	0. 020	0. 002	0. 002	0. 002
Silver—minimum percent	-------	. 002	-------	-------	-------	-------	-------
Copper—maximum percent	. 0015	. 080	. 080	. 080	. 0025	. 0025	. 04
Copper—minimum percent	-------	. 040	. 040	. 040	-------	-------	-------
Silver and copper together maximum percent	. 0025	-------	-------	-------	-------	-------	-------
Arsenic—maximum percent	. 0015	-------	-------	-------	-------	-------	-------
Antimony and tin together maximum percent	. 0095	-------	-------	-------	-------	-------	-------
Arsenic, antimony and tin together maximum percent	-------	. 002	. 002	. 015	. 015	. 015	. 015
Zinc—maximum percent	. 0015	. 001	. 001	. 002	. 002	. 002	. 002
Iron—maximum percent	. 002	. 002	. 002	. 002	. 002	. 002	. 002
Bismuth—maximum percent	. 05	. 005	. 025	. 10	. 15	. 25	. 005
Lead (by difference)—minimum percent	99. 94	99. 90	99. 90	99. 85	99. 85	99. 73	99. 93

[1] Corroding lead is a designation that has been used for many years in the trade to describe lead which has been refined to a high degree of purity.
[2] Chemical lead has been used for many years in the trade to describe the undesilverized lead produced from southeastern Missouri ores.
[3] Acid lead is made by adding copper to fully refined lead.
[4] Copper lead is made by adding copper to fully refined lead.
[5] Common desilverized leads A and B are designations that are used to describe fully refined desilverized lead.
[6] Soft undesilverized lead is used in the trade to describe the type of lead produced from ores of the Joplin, Mo., district.

TECHNOLOGY

Geology

The common lead minerals are galena (lead sulfide), cerussite (lead carbonate), and anglesite (lead sulfate). Galena is the most abundant lead mineral found in deposits that have been exploited in the United States. Galena is commonly associated with zinc, silver, gold, and iron minerals. However, in a few districts the ore is characterized by simple mineralization, with lead minerals present to the virtual exclusion of other ore minerals. A noteworthy example is southeastern Missouri, where the lead ores are usually composed of galena in an essentially nonmetallic gangue, with relatively little silver, zinc, copper, or other valuable metals present.

The more important economic deposits in the United States occur either as cavity fillings or replacements. The origin of the mineralization in the cavity filling and replacement deposits is similar. The theory that the mineral-bearing solutions were derived from a deep-seated igneous mass is most widely accepted today. Examples of the cavity-filling deposit are the San Juan, Colo., and the Upper Mississippi Valley districts. Replacement deposits are classified further as follows: massive, as at Leadville, Colo., and Bingham and Tintic, Utah; lodes, as at Park City, Utah, and in the Coeur d'Alenes, Idaho; disseminated, as in the Tri-State district and in southeast Missouri; and metasomatic, as represented by the Central district, New Mexico.

Prospecting and Exploration

Lead prospecting and exploration were relatively simple in the 18th and 19th centuries, when such important districts as southeast Missouri, the Tri-State, Upper Mississippi Valley, and Austinville, Va., were first brought into production. As the easily discovered, relatively shallow, ore bodies were depleted, it became necessary to employ new prospecting techniques involving careful geologic mapping of rock formations and structural features that control or may control ore deposition. Through intensive study the mining geologist and exploration engineer have increased their knowledge of the fundamentals of replacement, structural control, contact metamorphism, zonal distribution, structural barriers, wall-rock alteration, oxidation, and tectonics both before and after ore deposition and are utilizing this knowledge in guiding prospecting and exploration. Utilizing geophysical (*17*) and geochemical (*7*) techniques, largely pioneered in petroleum exploration, geologists and engineers have worked intensively seeking anomalous conditions indicative of conditions favorable to economic mineralization. These techniques have recently been used with much success to find anomalies that lead to ore discoveries in the Little River area of New Brunswick, Manitouwadge area of Ontario, and southeast Missouri.

Mining

Lead deposits amenable to open pit methods are uncommon but have found limited applica-

tion in the Tri-State district and Washington and more recently at Santander, Peru. Underground methods employing either open or supported stopes are used in most lead mines. Underground stoping includes block caving, room-and-pillar with and without rock bolts, shrinkage, cut-and-fill, and timbered stoping methods.

Improvements in mining practice in the past 40 to 50 years have been based largely on the development and extensive use of power equipment. Power shovels, scrapers, and mucking machines have replaced hand loading. Transportation also has undergone great changes; hand tramming and mule power have been replaced by motor trains operating on heavy-gage track. More recently trackless mining, which utilizes electric- or diesel-powered units, is finding wide usage in the lead and lead-zinc mines of Washington, the Tri-State (*4*), the Upper Mississippi Valley (*1*), and southeast Missouri (*3*, *8*). Mechanization is well adapted to the high backs, single-level mines that characterize so many of the lead and lead-zinc replacement ore bodies.

Other changes in equipment that have done much to improve mine output per man-shift include electric cap and floodlights at working faces, improved ventilation (including air conditioning), more efficient pumps, and powerful, lightweight rock drills using alloy steel or tungsten carbide bits.

Milling

Simple lead ores, such as coarsely disseminated lead or zinc-lead minerals occuring with a low-specific gravity gangue, are treated in heavy-medium equipment, jigs, and on tables after being crushed and rolled in closed circuit with screens or classifiers to give properly sized feed. Bulk or differential flotation of the slime products (*5*) or of a reground middling product completes the flowsheet. Ores of this kind are common in the mines of the Mississippi Valley and Eastern United States, but in some instances the ores are concentrated wholly by flotation.

Complex sulfide ores such as those of the Western United States consist of disseminated mixtures of fine-grained lead and zinc sulfides, usually accompanied by pyrite, copper sulfides, and gold and silver in a quartz or quartz-calcite gangue. Such ores may be complicated further by partial oxidation of the sulfides and presence of high-specific-gravity gangue minerals, such as barite, siderite, and rhodochrosite. The usual procedure on such an ore is to crush and grind in closed circuit with classifying equipment to a size at which the ore minerals are freed from the gangue minerals. When the ore minerals are interlocked, the usual practice is to make a bulk sulfide concentrate, followed by regrinding and selective flotation.

Low capital and operating costs have extended the field of the sink-float method to include pretreatment of certain ores, permitting upgrading of ores diluted by nonselective mining methods. Present milling practices result in recovery of 85 to 94 percent of the sulfide lead and up to about 88 percent of the oxidized lead. Sulfide losses consist largely of the extremely fine particles, and although much research has been done and improvements have been made in the recovery of fines the results are still unsatisfactory.

Smelting

Lead is recovered from its ores almost exclusively by smelting in blast furnaces or ore hearths employing carbon fuels. Ores or concentrates that contain few impurities may be reduced to metal in roasting hearths. Air is used to oxidize the sulfides and coke or coal to reduce the oxides. The ore hearth practice is followed at Galena, Kans., smelter, where (Newman) roasting hearths are used primarily in manufacture of lead oxide. The same process is employed at the New Broken Hill Smelter of Rhodesia, but is being replaced by blast-furnace methods.

In preparing the charge for blast-furnace smelting, the sulfur in the ores and concentrates is removed by a roasting-sintering process, usually on a Dwight-Lloyd sintering hearth (*10*). The sintering equipment eliminates most of the sulfur and produces a blast-furnace feed of desirable characteristics from the mechanically mixed concentrate, undersized sinter particles, and byproduct dusts and fumes collected in the smelter. Normally the charge to the lead blast furnace consists of lead sinter, coke, fluxes (such as silica and lime), and some lead-bearing furnace byproducts (*13*). Air is blown through the charge burning the coke to CO and CO_2 and producing a temperature of approximately 1,400° C. The carbon monoxide formed and the hot solid carbon reduce the oxidized lead compounds to bullion, which is tapped from the bottom or crucible of the furnace. Any copper, iron, cobalt, or nickel present in the ore combines with sulfur in the charge to form mattes which are tapped from the front of the blast furnace for subsequent treatment. Zinc present in the ore accumulates in the slag. When such slags contain 6 percent or more zinc, they are retreated in slag-fuming furnaces to recover the zinc and any remaining lead. The lead bullion contains precious metals present in the ore and metallic impurities which are recovered in the

refining operation. The recent development by Imperial Smelting Corp., Ltd., England, has gained favor in the treatment of complex lead-zinc ores. The three products of the furnace are zinc metal, lead bullion, and matte. A furnace of this type is presently operating in England, Australia, and Rhodesia, and several are in construction or planned throughout the world (*12, 14*).

Lead recoveries at primary lead smelters are usually about 97 to 99 percent of the lead contained in the ore and offer a relatively small margin for improvement. Recent modernization programs center largely on charge preparation, roasting, dust collection, and material handling within the plants (*14*). Such programs have more than doubled the productive capacity of lead blast furnaces since 1925.

Refining

Lead bullion from smelters operating on the ores of the Mississippi Valley, termed "chemical lead," is pure enough for most commercial uses without further refining. Lead bullion produced from western and most foreign ore contains enough gold and silver to make extraction profitable. It also contains various base-metal impurities that must be removed before the lead is marketable for end use. The sequence of processes for softening and desilverizing lead bullion and the recovery of byproducts is subject to many variations in practice.

Softening consists of the removal of copper, tin, antimony, and arsenic in a drossing or refining kettle. The copper is removed by holding the bullion just above the melting point and skimming copper dross from the surface. Agitation, with addition of elemental sulfur, causes the remaining copper to rise to the surface as a black copper sulfide powder, which is skimmed off. After copper drossing, the temperature of the bullion is raised and the bath agitated to induce surface oxidation. The tin, arsenic, and antimony are oxidized, and the oxides (being insoluble in the bath) rise to the surface with some lead oxide, which is skimmed off. The softened bullion usually is desilverized by the Parkes process of stirring metallic zinc into the bullion. Gold and silver, in that order, combine with the zinc and the resultant alloys on cooling rise to the surface and are skimmed off as gold and silver zinc crusts. The zinc remaining in the lead after desilverizing is removed by vacuum distillation or with caustic by the Harris process. If bismuth above acceptable limits is present, the bullion must be refined by the Betts electrolytic process, as at Trail, British Columbia, and East Chicago, Ind., or be removed by the Kroll-Betterton process after desilverization (*13*).

USES

An unusual combination of physical and chemical properties has given lead a wide range of industrial uses. The most important of these properties are as follows: Softness and extreme workability, high specific gravity, desirable alloying properties, low metal cost and high recoverability, high boiling point and low melting point, good corrosion resistance, and impenetrability by short wave radiation (*2, 9, 11*).

The principal uses of lead are for storage batteries, tetraethyl lead, cable covering, paint pigments, building construction, ammunition, and various alloys, chiefly solder, bearing metals, and type metal. Two of the larger uses—paint pigments and tetraethyl fluid—are dissipative. The greater part of the lead used in other forms is recoverable and eventually returns to supply as secondary metal.

Lead is used in the form of pure metal as in calking lead, cable covering, weights, foil, and sheets. It is widely utilized alloyed with certain metals, principally antimony and tin, in varying quantities to achieve the desired hardness, strength, friction, and melting-point characteristics desired for the specific application. The more common lead-base alloys are—bearing alloys, type metals, solders, ammunition and terneplate. The principal alloys of lead and content of other alloying elements are listed in table 3. Lead containing 6 to 12 percent antimony and commonly called antimonial lead is used chiefly in storage battery grids. Fusible alloys having controlled melting points ranging from 96° to 47° C are eutectic compositions of lead and various combinations of bismuth, tin, antimony, and cadmium. These alloys have expanding use in fire protection systems, precision casting, forming, and numerous other industrial applications. Lead is added to some copper-base alloys as well as to aluminum and steel to improve machinability. Lead is an ingredient in some greases and wire-rope lubricants to lessen frictional wear in especially abrasive service.

Large quantities of lead are consumed in the production of litharge, red lead, white lead, lead chromate, and basic lead sulfate. Litharge is used principally in storage batteries in both the positive and negative plates, either alone or mixed with finely divided metallic lead. Smaller quantities are used in the manufacture of ceramics, lead chromate, varnish, insecticides, oil refining, and rubber. Red lead is

used chiefly in storage batteries mixed with litharge and metallic lead in the positive plates and in paints. White lead is used almost exclusively as a paint pigment. Basic lead sulfate is used extensively in leaded zinc oxide and as a stabilizer in certain plastics.

TABLE 2.—*Lead use pattern in 1963*

Use	Percent of total
Batteries (grids and oxides)	38
Tetraethyl fluid	17
Cable covering	5
Calking lead	7
Red lead and litharge	6
Solder	6
Ammunition	4
Type metals	2
Sheet lead	2
Pipes, traps, etc.	2
Other uses	11
Total	100

An important but small use is for shielding against certain types of dangerous radiation, chief among these being gamma rays. Where space is at a premium and utmost radiation protection is paramount, lead is prescribed. Another advantage is that lead does not become contaminated and may be used continuously without becoming radioactive and emitting its own harmful rays. For this reason it is important that lead for shielding purposes be free of impurities, particularly those that may become radioactive upon exposure to high-energy radiation. The atomic reactors operated by the Atomic Energy Commission employ combinations of concrete, lead, cadmium, and space to protect operating personnel from all types of radiation, including alpha, beta, gamma, and neutron rays. The two last are particularly dangerous because of their ability to ionize matter and hence injure living tissue. Lead is particularly effective in absorbing gamma rays, whereas cadmium or a hydrogenous material, such as paraffin or water, is used to shield against neutrons; but since gamma rays are emitted when neutrons are absorbed, it is necessary to stop the gamma ray with lead shielding. Lead containers used in handling and shipping radioactive isotopes at the Brookhaven National Laboratories total over 1,000 tons.

Of the chemicals containing lead, tetraethyl lead is the most important. Tetraethyl lead is a colorless, heavy liquid with formula $Pb(C_2H_5)_4$ and containing 64 percent lead. It is the active ingredient of the principal antiknock compounds added to gasoline to improve their antiknock qualities and efficiency. Premium gasoline for automobiles may contain 2 to 4 cubic centimeters of tetraethyl lead per gallon (about 3 grams of lead) while most other gasolines contain up to 1.5 cubic centimeters per gallon. The improved efficiency of gasoline as a result of this additive results in an economy in the quantity of fuel used.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

About 60 percent of the U.S. mine production of lead is mined as a coproduct with zinc and from this mixed ore in addition to the lead and zinc, important quantities of byproduct silver, gold, copper, cadmium, antimony, bismuth, arsenic, and tellurium are recovered. Although most of the zinc and sometimes the copper occurring in complex ores are differentially concentrated, the lead concentrate produced commonly contains zinc and copper, as well as the other byproduct metals listed above. These are recovered in lead smelting-refining. In fact if it were not for the association of precious metals, bismuth, antimony and some other elements with lead ores and recovery in the late stages of lead refining at a comparatively low additional cost, the world supply of these metals would be substantially lower in quantity and higher in cost.

ALTERNATE MATERIALS

Alternate materials are available which provide to a varying degree the properties and characteristics required in the classic applications of lead. Substitution of these materials depends on industrial factors of price, availability, dependability, and workability as well as many secondary considerations.

In the storage battery industry, the largest consumer of lead, there are alternate combinations of materials used in specialized applications in preference to the lead-acid cell such as cadmium, mercury, nickel, and silver. These materials are, however, limited in quantity and certain electrical characteristics when compared with the automotive and industrial requirements for storage battery power. The fuel cell may supplant in some specialized uses the electrical energy function of storage batteries.

Lead in gasoline antiknock additives constituting the second largest application of lead in the form of tetraethyl and tetramethyl presently does not have an economical alternate. Nickel, as well as other metallics, can perform a similar function in high-impression fuels. These materials have not, however, other necessary characteristics to constitute a large alternate potential. Large-scale substitution of diesel or turbine engines using low-octane fuels for the high-compression gasoline engine offers

a future possibility of reduced gasoline additive requirements.

Cable covering, the third largest application of lead, is an application in which alternate materials have substantially replaced lead. Polyethylene and combinations of metallic and organic materials are used as moisture insulation in underground power and communication cables. Oil and gas filled steel pipe has substituted for lead sheathing in some installations. The chemical inertness and corrosion resistance of lead along with flexibility, long life, and low-temperature extrusion and bonding, however, maintains the desirability of lead sheathing for extremely corrosive applications.

The development of materials replacing lead in paint pigments has proceeded rapidly and in many instances, especially interior and house paints, lead has been completely replaced by titanium and zinc pigments. As a basic paint for rust and corrosion protection, lead base paints are still preferred.

In construction applications, lead is competitive with many alternate materials. Synthetic seals have substituted for calking lead and alternate methods of connecting plastic and cement-asbestos pipe have reduced the use of lead in plumbing. Stainless steel, titanium, plastic, and cement are alternate materials in corrosive chemical construction. Development of new materials and methods continue in radiation shielding, vibration dampening and soundproofing.

The use of tetraethyl for aviation fuel has been substantially reduced by the development of kerosine and low-octane gasoline-burning straight jet and turbojet engines. Catalytic reformed gasolines of high-octane rating and inherent antiknock qualities are competitive in automobile fuels. The only competing additive that appears to have use potential is tetramethyl lead, quite similar in lead content and manufacture to those of tetraethyl lead.

TABLE 3.—*Principal alloys employing lead as a primary ingredient*

Alloy	Typical use	Percent content of alloying element		
		Antimony	Tin	Other
Cable lead	Cable sheathing	0–1. 0		0–0. 1 Te, 0–.03 Ca.
Hard lead	Pipe and sheet	1. 0–4. 0		
6–8 percent antimonial lead.	High-strength pipe and sheet.	6. 0–8. 0		
Grid metal	Battery plates	5. 0–12. 0		
Silver lead solder	Coating and joining metals.		1. 0	1.50 Ag.
5–95 soft solder	do		5. 0	
20–80 soft solder	do		20. 0	
50–50 soft solder	do		50. 0	
Lead-base tin babbitt	Bearing metal	10. 0–15. 0	5–10	0–1.0 Ca, 0.009 Li.
Arsenical lead-base babbitt.	Heavy-duty bearing metal.	12. 5–15. 0	0. 75–1. 0	1.0–3.0 As.
Type metal	Type	2. 5–25. 0	2. 5–20. 0	
Fusible alloys	Low melting fuses		8. 0–97. 0	45–60 Bi, 5–40 Cd, Ag, Zn, and In.
Terne metal	Plating steel sheets		2–2.5 or 10.0–25.0	
Leaded brasses and bronzes.	Machined parts		1. 0–10. 0	66–88 Cu, 2–30 Zn.

SECONDARY SOURCES AND RECOVERY

The United States has a large reserve of recoverable lead-in-use. The quantity is estimated to be in the order of 4 million tons of recoverable lead of which about 1 million tons is in lead storage batteries, 2 million tons in power and telephone cable coverings, and over 1 million tons in railway car bearings, lead pipe, sheet lead, and type metal. This in-use reserve provided the secondary industry with scrap yielding an average of 462,000 tons of recoverable lead annually for 1959–63. Table 4 presents the statistics of secondary lead recovery in 1962 and 1963.

TABLE 4.—*Lead recovered from scrap processed in the United States, by kind of scrap and form of recovery*

[Short tons]

Kind of scrap	1962	1963	Form of recovery	1962	1963
New scrap:			As soft lead:		
Lead-base	44, 803	59, 577	At primary plants	1, 842	3, 741
Copper-base	5, 586	6, 094	At other plants	116, 626	130, 788
Tin-base	529	611			
Total	50, 918	66, 282	Total	118, 468	134, 529
Old scrap:			In antimonial lead [1]	229, 392	244, 797
Battery-lead plates	252, 593	272, 412	In other lead alloys	87, 243	92, 203
All other lead-base	124, 277	135, 844	In copper-base alloys	9, 019	21, 878
Copper-base	16, 409	18, 928	In tin-base alloys	80	64
Tin-base	5	5			
Total	393, 284	427, 189	Total	325, 734	358, 942
Grand total	444, 202	493, 471	Grand total	444, 202	493, 471

[1] Includes 3,693 tons of lead recovered in antimonial lead from secondary sources at primary plants in 1962 and 7,672 tons in 1963.

RESERVES

Lead-ore deposits are widely distributed throughout the world with commercially significant resources in some 50 individual countries. The more important reserves are in Australia, Canada, China, Mexico, Morocco, Peru, South-West Africa, United States, U.S.S.R., and Yugoslavia.

Information on reserves at the individual mining operations is obscured by individually applicable factors of economic minability and confidentiality as well as the normal tendency to maintain exploration and development only to the extent necessary to replace the ore mined. Reserves are, however, being added by new discoveries and extensions of presently producing deposits generally at a rate in excess of the lead produced. Since 1950, prospecting, exploration, and development in Canada has indicated some 6 million tons of lead in lead-zinc ores in the Pine Point, Bathurst, and Timmins mining districts. Exploration and development in Ireland and Yugoslavia have added substantial reserves, and the new south-central lead belt of Missouri is indicated to be a major addition to the U.S. reserve. Australia, South-West Africa and Peru are expanding reserves at presently operating mines.

Considering these developments and prior estimates, the measured and indicated lead reserves of the world are 50 million tons, equivalent to some 20 years output at current world levels. The reserve of inferred lead in ore is undoubtedly as large or larger.

Of the measured and indicated lead reserves, North America has about 37 percent or 18.7 million tons. Canada leads with 9 million tons followed by the United States with 6 million tons and Mexico with 3.5 million tons. The 3 million ton reserve of South America is mostly in Peru with other reserves in Argentina, Brazil, and Bolivia. African reserves of 4 million tons are primarily in South-West Africa and Morocco, with Algeria also contributing. Australia has substantial reserves of 6 million tons in the Broken Hill and Mt. Isa areas. Eastern European reserves are estimated at 10.1 million tons, mainly in the U.S.S.R. but also in each of the satellite countries. Yugoslavia, West Germany, Italy, Spain and Sweden account for the larger portion of the 5.6-million ton reserves of Western Europe. Asian reserves of 2.6 million tons are divided among Burma, China, India, Iran, Japan, North Korea, North Viet-Nam, Turkey—with China, Japan, and Burma the major areas.

CONSERVATION

Lead is so nearly indestructible that conservation is relatively simple. Almost all lead used except that in chemicals (including tetraethyl), pigments, and galvanizing is nondissipative and, except for uneconomic collection of some products, will eventually be returned to the secondary smelters for reclamation and reuse.

SOURCES OF STATISTICAL INFORMATION

Statistics on domestic and world mine and smelter production, domestic consumption of lead metal and scrap, stocks, shipments, and smelter average sales price are collected and

published by the Bureau of Mines. These data are supplemented by shipment-by-use figures published by the Lead Industries Association and by refinery production shipments and stocks compiled by the American Bureau of Metal Statistics. The Bureau of the Census conducts a census of the mineral industry of the United States every 5th year. Such studies provide valuable general information on productivity and costs. The Bureau of the Census also reports monthly import-export data for the United States. The International Lead and Zinc Study Group and the Organization for Economic Cooperation and Development collects and publishes statistics on world mine and metal production, consumption, and stocks.

TABLE 5.—*Supply and distribution of lead in the United States*

[Thousand short tons]

Year	Supply					Distribution		
	Primary lead production from—		Secondary production	Imports of metal	Total	Consumption	Exports of metal	Total
	Domestic materials	Foreign materials						
1954–58 (average)	322	180	476	299	1,277	1,128	2	1,130
1959	225	116	451	263	1,055	1,091	3	1,094
1960	229	154	470	206	1,059	1,021	2	1,023
1961	288	161	453	257	1,159	1,027	2	1,029
1962	246	130	444	257	1,077	1,110	2	1,112
1963	240	155	493	227	1,115	1,163	1	1,164

PRODUCTION, CONSUMPTION, AND TRADE

U.S. mine production of primary lead in 1963 was about 253,000 tons, approximately 9 percent of the world production. Mine production supplemented by imports of concentrates and bullion provided feed for the domestic refinery output of 395,000 tons, approximately 14 percent of the world primary smelter production. Primary production was further supplemented with secondary lead output and with imports of metal to meet the U.S. requirement of 1.16 million tons in 1963. Table 5 lists elements of supply and distribution for 1954–63.

World production of lead during 1954–62 was well in excess of world requirements, and large stocks were accumulated by primary producers, especially in the United States (*18*). In 1958, the U.S. Tariff Commission found imports of lead and of zinc to be threatening economic injury to the domestic industry. The President, on September 22, 1958, imposed import quotas effective October 1, 1958, which limited unmanufactured lead-ores, concentrates, bullion, and metal to 80 percent of the average annual imports from foreign countries during 1953–57. These quotas have constituted the ceiling for lead imports for consumption except during 1961–62, when approximately 104,000 tons of refined lead was obtained by government barter transaction with Canadian and Australian producers.

Domestic lead consumption, after suffering a major recession during 1957–61, recovered substantially in 1962 and increased again in 1963. The major lead outlets, storage batteries and gasoline additives, are for transportation. The adoption of jet engines on a large percentage of commercial and military aircraft substantially reduced the lead requirements for air transport, but the increasing number of automobiles and trucks has increased consumption in gasoline additives to record level. The number of vehicles on the road and the distance traveled are a major determinate of lead consumption. Other outlets of lead are associated mainly with construction and maintenance and have shown less fluctuation over the years, although trending downward in quantity. In 1963, the U.S. consumption of primary lead including domestic smelter production and imports of metal for consumption was approximately 23 percent of world primary production. The details of U.S. consumption are shown in table 7 and table 8.

World trade in lead is primarily in the form of concentrates and metal. Countries producing ore in excess of smelter requirements, notably Peru, Republic of South Africa, Canada, Australia, and Bolivia, are suppliers to the industrial countries having negligible or deficient output in relation to smelting capacity such as the United Kingdom, Belgium-Luxembourg, West Germany, France, and Japan. Several countries, notably Mexico, Australia, Canada, Yugoslavia, and Peru, have smelting capacity in excess of domestic metal requirements and export metal to the industrialized countries. The United States is an importer of both lead concentrates and lead metal from all of the the previously mentioned countries. Com-

TABLE 6.—*Mine production of recoverable lead in the United States, by States*

[Short tons]

State	1954–58 (average)	1959	1960	1961	1962	1963
Arizona	10,906	9,999	8,495	5,937	6,966	5,815
Arkansas		38				
California	4,766	227	440	103	455	823
Colorado	17,720	12,907	18,080	17,755	17,411	19,918
Idaho	64,605	62,395	42,907	71,476	84,058	75,759
Illinois	3,238	2,570	3,000	3,430	3,610	2,901
Kansas	4,544	481	781	1,449	970	1,027
Kentucky	247	409	558	656	743	831
Missouri	122,783	105,165	111,948	98,785	60,982	79,844
Montana	14,445	7,672	4,879	2,643	6,121	5,000
Nevada	4,569	1,357	987	1,791	771	1,126
New Mexico	3,327	829	1,996	2,332	1,134	1,014
New York	1,216	481	775	879	1,063	1,009
North Carolina	5		424	318	219	62
Oklahoma	10,311	601	936	980	2,710	3,192
Utah	45,961	36,630	39,398	40,894	38,199	45,028
Virginia	3,286	2,770	2,152	3,733	4,059	3,500
Washington	10,738	10,310	7,725	8,053	6,033	5,374
Wisconsin	1,698	745	1,165	680	1,394	1,116
Other States	8		23	27	58	30
Total	324,373	255,586	246,669	261,921	236,956	253,369

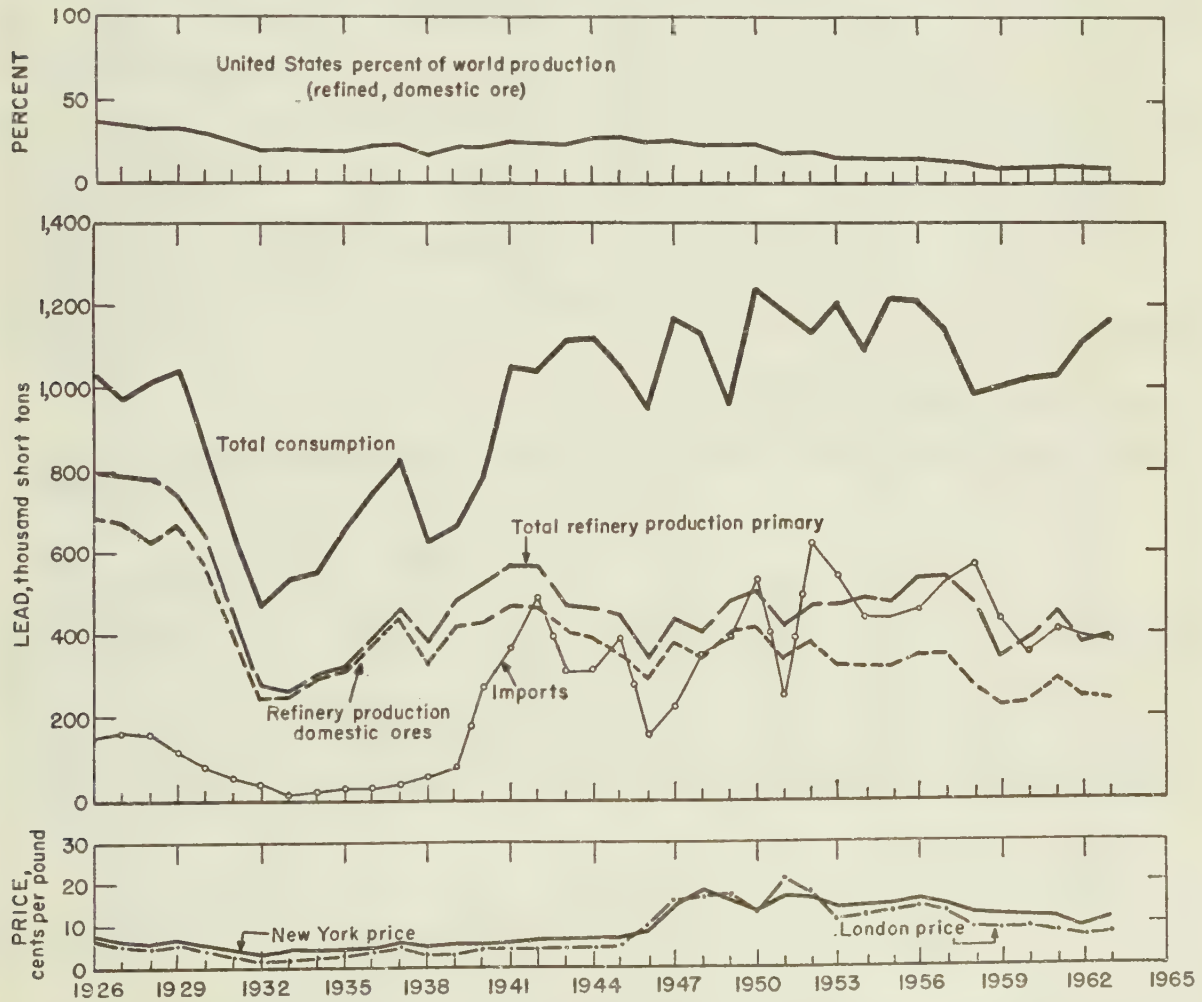

FIGURE 1.—Trends in the Lead Industry in the United States. Consumption Includes Primary Refined, Antimonial, and Secondary Lead, and Lead in Pigments Made Directly From Ore. Imports are Factored to Include 95 Percent of Lead Content of Ores, Mattes, and Concentrates and 100 Percent of Pigs, Bars, Base Bullion, and Scrap.

munist nation trade is principally between Communist countries, although varying quantities of lead concentrates are purchased and sales of metal made in trade with the free world (*2*).

For well over a century there has been a tariff on lead ranging from a low of 15 percent ad valorem to a high of 3 cents per pound, except for periods when such tariffs were suspended by act of Congress.

The statutory rate of duty under the Tariff Act of 1930 was 1½ cents per pound on lead content of ores flue dust, and matte and 2⅛ cents per pound on lead content of bullion, pigs and bars, antimonial lead, drosses and scrap. On June 6, 1951, pursuant to concessions granted in the General Agreement on Tariffs and Trade (GATT) these duties were reduced 50 percent to ¾ of a cent and 1 1/16 cents, respectively. The statutory rate is, however, currently applicable to imports from those communist controlled countries designated by the President.

New Tariff Schedules of the United States (TSUS) effective August 31, 1963, revised item designations but did not modify applicable tariff rates. Table 14 sets forth the schedules presently in effect.

TABLE 7.—*Lead consumption in the United States, by products*

[Short tons]

Product	1962	1963	Product	1962	1963
Metal products:			Pigments—Continued		
Ammunition	47,779	49,894	Pigment colors	11,660	11,767
Bearing metals	16,472	21,713	Other [1]	3,892	7,813
Brass and bronze	20,607	21,943			
Cable covering	56,676	57,707	Total	102,968	99,075
Calking lead	72,648	76,308			
Casting metals	7,355	7,856	Chemicals:		
Collapsible tubes	11,972	14,832	Gasoline antiknock additives	168,926	192,811
Foil	3,720	3,952	Miscellaneous chemicals	2,715	632
Pipes, traps, and bends	19,819	20,100			
Sheet lead	28,540	26,495	Total	171,641	193,443
Solder	66,878	67,945			
Storage batteries:			Miscellaneous uses:		
Battery grids, posts, etc.	217,525	222,286	Annealing	5,306	4,847
Battery oxides	202,381	216,795	Galvanizing	1,146	1,631
Terne metal	1,402	1,983	Lead plating	236	220
Type metal	26,760	26,069	Weights and ballast	10,330	12,207
Total	800,529	835,878	Total	17,018	18,905
			Other, unclassified uses	17,479	16,057
Pigments:					
White lead	11,091	8,846	Grand total [2]	1,109,635	1,163,358
Red lead and litharge	76,325	70,649			

[1] Includes lead content of leaded zinc oxide and other pigments and chemicals.
[2] Includes lead which went directly from scrap to fabricated products.

TABLE 8.—*Lead consumption in the United States in 1963, by class of products and types of material*

[Short tons]

Product	Soft lead	Lead in antimonial lead	Lead in alloys	Lead in copper-base scrap	Total
Metal products	206,311	86,534	47,368	16,451	356,664
Storage batteries	220,860	218,214	7		439,081
Pigments	94,912	178			95,090
Chemicals	193,443				193,443
Miscellaneous	10,915	7,987	3		18,905
Unclassified	13,719	1,525	565		15,809
Total	740,160	314,438	47,943	16,451	[1] 1,118,992

[1] Excludes 40,381 tons of lead that went directly from scrap to fabricated products and 3,985 tons of lead contained in leaded zinc oxide and other pigments and chemicals.

TABLE 9.—*U.S. imports [1] of lead, by countries*

[Short tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963
Ore, flue dust, and matte (lead content):						
North America:						
Canada	30,368	32,226	26,473	34,361	27,728	23,634
Guatemala	5,756	153	1,809	9,817	2,135	305
Honduras	2,779	3,639	4,906	5,512	[2] 4,965	6,809
Mexico	2,771	489	1,249	1,166	1,180	1,071
Other	1,089	195				
Total	42,763	36,702	34,437	50,856	[2] 36,008	31,819
South America:						
Bolivia	15,794	11,221	9,021	11,370	8,242	9,791
Chile	220	113	1,283	610		
Colombia	639	570	705	722	439	9
Peru	52,929	36,777	36,300	28,970	[2] 32,999	43,950
Other	320	53	103			
Total	69,902	48,734	47,412	41,672	[2] 41,680	53,750
Europe	246	221	222	300	280	
Asia:						
Philippines	1,794	310	228	238	57	23
Other	197	25	504		181	244
Total	1,991	335	732	238	238	267
Africa:						
Morocco [3]			5,238			
South Africa, Republic of [4]	42,884	27,879	39,352	34,089	33,881	34,273
Other	9					
Total	42,893	27,879	44,590	34,089	33,881	34,273
Oceania: Australia	29,259	24,963	18,299	20,631	26,644	27,633
Total ore, flue dust, and matte	187,054	138,834	145,692	147,186	[2] 138,631	147,742
Base bullion (lead content):						
North America	8	34	254	362	5	851
South America	115	46	39	60	2,080	2,647
Europe				[5]		2
Asia	[5]					
Oceania					2,514	1,937
Total base bullion	123	80	293	422	4,599	5,437
Pigs and bars (lead content):						
North America:						
Canada	36,019	41,533	26,088	54,717	56,807	29,619
Mexico	92,995	86,827	69,930	81,328	65,892	74,469
Other	4	324	9	3		
Total	129,018	128,684	96,027	136,048	122,699	104,085
South America:						
Peru	31,113	29,311	25,197	26,195	22,115	23,486
Other	349					36
Total	31,462	29,311	25,197	26,195	22,115	23,522
Europe:						
Belgium-Luxembourg	1,900	1,503	610		2,980	11,235
Germany, West	1,226	2,893	551	842	914	277
Spain	8,057	9,395	4,115	8,529	4,104	7,694
United Kingdom	2,810	988	7		335	3,555
Yugoslavia	38,015	32,731	30,027	30,347	31,909	31,063
Other	2,659	4,872	1,388		12	
Total	54,667	52,382	36,698	39,718	40,254	53,824
Asia	13					
Africa: Morocco [3]	[6] 10,068	[7] 5,384	[7] 1,328			
Oceania: Australia	73,936	47,655	46,783	54,891	72,133	45,596
Total pigs and bars	299,164	263,416	206,033	256,852	257,201	227,027
Reclaimed, scrap, etc. (lead content):						
North America:						
Canada	4,197	2,251	4,059	1,441	1,279	3,243
Mexico	4,328	1,293	1,054	2,294	688	55
Other	966	245	160	45	186	162
Total	9,491	3,789	5,273	3,780	2,153	3,460
South America:						
Peru	138	[5]				
Venezuela	377					
Other	11	120				
Total	526	120				

See footnotes at end of table.

TABLE 9.—*U.S. imports [1] of lead, by countries*—Continued

[Short tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963
Europe:						
Belgium-Luxembourg	140					
Denmark	273					
Germany, West	115	1	1		(5)	1
Netherlands	54				17	12
Other	198		4	2		
Total	780	1	5	2	17	13
Asia:						
Japan (including Nansei and Nanpo Islands)	8	18	5		2	
Other	14					
Total	22	18	5		2	
Oceania: Australia	1,732	4,351	2,355	1,160	149	5,402
Total reclaimed, scrap, etc	12,551	8,279	7,638	4,942	2,321	8,875
Grand total	498,892	410,609	359,656	409,402	[2] 402,752	389,081

[1] Data are general imports; that is, they include lead imported for immediate consumption plus material entering the country under bond.
[2] Revised figure.
[3] French Morocco before Jan. 1, 1957.
[4] Union of South Africa before Jan. 1, 1962.
[5] Less than 1 ton.
[6] Includes material classified by the Bureau of the Census as being from Algeria but believed by Bureau of Mines to be from French Morocco.
[7] Includes 1,052 tons from the Federation of Rhodesia and Nyasaland in 1959 and 224 tons in 1960.

Source: Bureau of the Census.

TABLE 10.—*U.S. imports for consumption of lead, by classes* [1] [2]

Year	Lead in ores, flue dust or fume, and mattes, n.s.p.f. (lead content)		Lead in base bullion (lead content)		Pigs and bars (lead content)		Sheets, pipe, and shot		Not otherwise specified value (thousands)	Total value (thousands)
	Short tons	Value (thousands)	Short tons	Value (thousands)	Short tons	Value (thousands)	Short tons	Value (thousands)		
1954–58 (average)	203,206	[3] $49,957	103	$33	294,787	[3] $75,144	3,728	[3] $931	[3] $261	[3] $129,072
1959	136,526	27,035	34	19	262,632	54,667	3,608	850	586	84,461
1960	137,303	27,816	293	[4] 62	213,347	45,065	2,855	696	710	75,383
1961	136,780	24,332	236	[4] 51	247,427	45,881	2,845	641	807	72,304
1962	[5] 133,080	[5] 21,003	2,083	710	257,866	41,570	2,276	474	978	[5] 65,004
1963	134,445	21,436	3,758	1,792	220,398	40,226	2,429	513	792	66,768

[1] Excludes imports for consumption in bond and export, classified as "imports for consumption" by the Bureau of the Census.
[2] In addition to quantities shown (value included in total value), "reclaimed scrap, etc." imported as follows: 1954–58 (average): 12,564 tons, $2,746,134; 1959: 7,897 tons, $1,304,107; 1960: 5,598 tons, $1,034,141; 1961: 3,894 tons, $591,971; 1962: 2,078 tons, $269,101; 1963: 15,405 tons, $2,008,916.
[3] Data known to be not comparable with other years.
[4] Values for Peru in 1960 and Peru and Mexico in 1961 have been adjusted by the Bureau of Mines to reflect the value of lead.
[5] Revised figure.

Source: Bureau of the Census.

TABLE 11.—*U.S. imports for consumption of miscellaneous products containing lead*

Year	Babbitt metal, solder, white metal and other combinations containing lead [1]			Type metal and antimonial lead		
	Gross weight (short tons)	Lead content (short tons)	Value (thousands)	Gross weight (short tons)	Lead content (short tons)	Value (thousands)
1954–58 (average)	3,289	1,906	[2] $2,993	7,741	6,893	$2,222
1959	11,840	3,751	16,820	5,612	5,020	1,204
1960	9,274	1,512	16,024	4,560	3,915	970
1961	7,930	1,409	14,207	6,430	5,765	1,340
1962	2,438	1,030	3,443	8,576	7,512	1,393
1963	2,535	1,246	3,207	[2] 3,747	[2] 3,196	[2] 621

[1] 1960–62 data known to be not comparable with earlier years.
[2] Data known to be not comparable with other years.
[3] Due to changes in classification, effective Sept. 1, 1963, data no longer separately classified. January–August data tabulated.

Source: Bureau of the Census.

TABLE 12.—*World mine production of lead (content of ore) recoverable where indicated, by countries* [1] [2]

[Short tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963
North America:						
Canada	[3] 195,655	[3] 186,696	[3] 205,650	[4] 182,557	[4] 211,321	[4] 198,988
Cuba	73					
Greenland	[5] 7,625	11,633	7,635	10,104	892	
Guatemala [3]	7,596	6,381	9,432	9,458	1,067	825
Honduras	2,379	4,604	5,913	6,762	6,522	[6] 10,913
Mexico	212,491	210,188	210,177	199,877	213,074	209,425
United States [3]	324,373	255,586	246,669	261,921	236,956	253,369
Total	750,192	675,088	685,476	670,679	669,832	673,520
South America:						
Argentina	28,770	33,400	29,432	31,306	32,606	28,991
Bolivia (exports)	23,810	24,293	23,610	22,403	20,504	22,226
Brazil [7]	5,400	6,700	12,200	15,300	17,500	17,500
Chile	3,667	2,560	2,694	2,252	1,603	1,074
Colombia (U.S. imports)	639	570	705	722	439	9
Ecuador	119	118	119	122	137	181
Peru	138,716	[3] 127,003	[3] 145,097	[3] 150,353	[3] 141,290	163,468
Total	201,121	194,644	213,857	222,458	214,079	233,449
Europe:						
Austria [3]	5,596	5,906	5,758	6,051	5,855	5,504
Bulgaria	63,642	88,673	92,341	88,229	104,058	97,995
Czechoslovakia [7]	5,700	7,000	7,200	7,200	14,900	14,900
Finland	1,561	2,126	1,755	3,439	3,161	1,262
France	12,091	18,335	20,451	20,785	15,735	7,187
Germany:						
East [7]	6,800	7,700	7,700	7,700	8,300	8,300
West	73,260	57,882	54,919	54,453	54,710	57,143
Greece	6,839	11,023	10,141	12,787	14,550	[7] 14,550
Ireland	1,898	1,476	1,480	279		
Italy	56,267	56,655	54,525	52,612	45,463	36,266
Norway	1,157	2,487	2,780	2,524	3,417	3,858
Poland	38,272	39,022	43,211	42,108	36,156	42,659
Portugal	1,485	35	34	28	49	
Rumania [7] [8]	12,700	13,200	13,200	13,200	13,800	13,800
Spain	69,139	77,271	80,353	87,863	78,262	67,076
Sweden	38,217	53,322	60,963	70,518	74,737	77,051
U.S.S.R. [7]	285,000	[3] 350,000	[3] 360,000	[3] 390,000	[3] 390,000	[3] 390,000
United Kingdom	[3] 8,018	2,632	1,549	1,656	446	276
Yugoslavia	97,326	101,909	100,554	106,572	112,430	111,968
Total [7]	785,000	896,700	918,900	968,000	976,000	949,800
Asia:						
Burma	17,913	21,275	19,070	18,519	22,377	28,788
China [7]	38,600	77,000	88,000	99,000	99,000	110,000
India	3,309	5,292	4,991	4,478	5,065	4,758
Iran [7] [9]	17,900	16,500	16,500	16,500	11,000	11,000
Japan	33,357	39,844	43,577	51,015	58,924	58,115
Korea:						
North [7]	33,000	44,000	55,000	55,000	55,000	55,000
Republic of	960	256	1,012	1,014	1,558	2,113
Philippines	1,849	391	134	111	90	78
Thailand	4,025	1,455	2,028	2,437	2,600	2,496
Turkey	2,226	1,301	1,830	3,538	4,299	2,811
Total [7]	153,100	207,300	232,100	251,600	259,900	275,200
Africa:						
Algeria	11,481	12,173	11,529	10,337	9,964	8,841
Congo, Republic of	3,294	5,448	4,741	965	368	364
Morocco	98,098	101,082	104,444	97,299	99,323	81,000
Nigeria	226	424	223	7		
Rhodesia and Nyasaland, Federation of: Northern Rhodesia [8]	16,659	16,128	16,161	16,999	16,343	21,616
South Africa, Republic of	583	150	121	91	6	16
South-West Africa [10]	87,903	[3] 77,551	71,540	69,997	82,688	80,878
Tanganyika (exports)	4,514	6,401	6,927	387		
Tunisia	27,101	19,997	19,986	19,163	14,936	15,245
Uganda (exports)	110	60				
United Arab Republic (Egypt)	205	770	88	39	595	550
Total	250,174	240,184	235,760	215,284	224,223	208,510
Oceania: Australia	345,167	354,249	345,143	302,015	414,530	459,026
World total (estimate)	2,484,000	2,570,000	2,630,000	2,630,000	2,760,000	2,800,000

[1] Data derived in part from United Nations Statistical Yearbook, Yearbook of the American Bureau of Metal Statistics, and annual issues of the Statistical Summary of the Mineral Industry (Overseas Geological Survey, London), and Metal Statistics (Metallgesellschaft) Germany.

[2] This table incorporates some revisions. Data do not add exactly to totals shown because of rounding where estimated figures are included in the detail.

[3] Recoverable.

[4] Data for 1961, 1962, and 1963 not strictly comparable to previous years.

[5] Average annual production 1956–58.

[6] Exports.

[7] Estimate.

[8] Smelter production.

[9] Year ended March 21 of year following that stated.

[10] Includes lead content of lead-vanadium concentrates.

TABLE 13.—*World smelter production of lead by countries* [1] [2]

[Short tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963
North America:						
Canada	148,856	140,881	160,079	172,365	152,743	202,398
Guatemala	[3] 55		200	62	68	52
Mexico	223,805	206,134	205,263	194,476	208,447	205,217
United States (refined) [4]	502,149	340,886	382,436	449,486	376,024	394,732
Total	874,865	687,901	747,978	816,389	737,282	802,399
South America:						
Argentina	28,000	34,200	28,300	30,865	27,000	26,500
Bolivia (exports) [5]	1,798	250	119	4	138	
Brazil	4,882	6,091	10,997	13,809	15,758	[3] 15,400
Chile	185	892	661	529	280	243
Peru	68,985	62,619	81,726	84,253	75,356	91,577
Total	103,850	104,052	121,803	129,460	118,532	133,720
Europe:						
Austria [6]	13,035	13,610	13,717	13,605	13,417	10,783
Belgium [6]	99,664	97,489	102,190	110,110	102,681	108,507
Bulgaria	13,393	36,090	44,540	45,099	48,171	56,584
Czechoslovakia [3]	9,500	10,000	10,000	10,000	15,400	15,400
France	74,257	77,982	81,998	78,052	77,787	85,570
Germany:						
East [3] [6]	27,000	27,500	27,500	27,500	28,700	28,700
West	133,688	164,833	162,772	155,008	163,902	154,032
Greece	3,590	4,122	3,407	3,267	3,300	3,900
Italy	45,388	48,548	45,912	49,769	46,282	46,224
Poland	38,101	42,645	43,762	43,874	44,842	42,895
Portugal	1,157	876	998	1,663	2,227	1,129
Rumania [3]	12,700	13,200	13,200	13,200	13,800	13,800
Spain	69,690	75,497	78,464	85,678	79,666	65,973
Sweden	26,994	40,619	48,010	42,745	42,716	45,000
U.S.S.R [3]	285,000	350,000	360,000	390,000	390,000	390,000
United Kingdom	6,889	1,580	1,224	1,178	614	297
Yugoslavia	83,971	94,132	98,263	99,650	107,945	114,832
Total [3]	943,900	1,097,800	1,136,000	1,170,400	1,181,500	1,183,600
Asia:						
Burma	19,298	21,768	18,499	17,376	19,164	19,553
China [3]	28,000	66,000	77,000	95,000	95,000	99,000
India	2,919	4,363	4,128	4,039	3,140	3,899
Iran [7]	1,151	[3] 1,000	1,279	1,437	441	[3] 440
Japan	46,343	67,152	76,465	83,476	96,783	104,499
Korea: North [3]	13,000	22,000	33,000	45,000	45,000	45,000
Turkey [3]	[6] 2,070	509	518	698	702	2,073
Total [3]	112,800	182,800	210,900	247,000	260,200	274,500
Africa:						
Morocco	32,158	31,368	33,871	26,993	26,566	20,679
Rhodesia and Nyasaland, Federation of: Northern Rhodesia	16,659	16,128	16,161	16,999	16,343	21,616
Tunisia [5]	27,966	24,039	21,894	20,307	17,447	14,110
Total	76,783	71,535	71,926	64,299	60,356	56,405
Oceania: Australia:						
Refined lead	216,504	208,102	212,603	181,736	212,941	251,558
Pb content of lead bullion (for export)	49,562	56,347	59,050	53,861	81,883	90,341
Total	266,066	264,449	271,653	235,597	294,824	341,899
World total (estimate)	2,380,000	2,410,000	2,560,000	2,665,000	2,655,000	2,795,000

[1] Data derived in part from United Nations Statistical Yearbook, Yearbook of the American Bureau of Metal Statistics, and annual issues of Statistical Summary of the Mineral Industry (Overseas Geological Surveys, London), and Metal Statistics (Metallgesellschaft) Germany.

[2] This table incorporates some revisions. Data do not add exactly to totals shown because of rounding where estimated figures are included in the detail.

[3] Estimate.

[4] Figures cover lead refined from domestic and foreign ores; refined lead produced from foreign base bullion not included.

[5] Lead bars only; does not include lead contained in antimonial lead or in solders.

[6] Includes scrap.

[7] Year ended Mar. 21 of year following that stated.

TABLE 14.—*Unmanufactured lead and zinc articles rates of duty under the Tariff Schedules effective Aug. 31, 1963*

TSUS item number and article description	Rate under GATT	Statutory rate
602.10 All lead bearing ores [1]	0.75¢ per lb	1.5¢ per lb.
603.25 Lead dross [1]	1.0625¢ per lb	2.125¢ per lb.
624.02 Lead bullion [2]	1.0625¢ per lb	2.125¢ per lb.
624.03 Unwrought lead other than bullion.[1]	1.0625¢ per lb	2.125¢ per lb.

[1] Lead content.
[2] 99.6 percent of lead content.

SELF-SUFFICIENCY AND STRATEGIC CONSIDERATIONS

From 1925 through 1958 about 41 percent of the total U.S. supply of lead was from domestic mines, 34 percent from secondary sources, and the remaining 25 percent from imports. During 1959–63, under import controls, mine production amounted to 23 percent of the supply, secondary materials furnished 41 percent, and imports of lead metal proved 36 percent. In addition to heavy dependence upon imports of primary lead materials and metal since the beginning of World War II, the lead recovered in secondary operations was derived in part from imported scrap.

The United States is in a sound strategic position with relation to lead inasmuch as both the primary and secondary lead industry are well dispersed; the country is a next-door neighbor to Canada and Mexico, major lead-exporting countries; and because the strategic and long-term stockpile objectives have been met and substantial other quantities are held in the Government's supplemental stockpile. The Government holds in inventory a quantity of lead metal approximately equivalent to 1 year's consumption. On June 30, 1964, inventories totaled 1.4 million tons, of which 1.1 million was in the national (strategic) stockpile and 0.3 million was in the supplemental stockpile.

GOVERNMENT PROGRAMS

The Government regulated the lead industry during World War II and again in 1951–52 to provide adequate supplies for all essential purposes. In World War II measures were taken to increase imports greatly, expand or at least maintain domestic mine production, increase secondary recovery, decrease exports, and control consumption.

Lead was first recommended for stockpiling in May 1941, when the Office of Production Management proposed that the Metals Reserve Co. acquire 50,000 to 100,000 tons. Government stocks, built up largely from imports, increased monthly from 5,000 tons in August 1941 to a peak of 266,000 tons in April 1943. It was not until the latter part of 1944 that requirements necessitated continued withdrawal of large quantities of metal from the stockpile; by July 1945 the inventory had decreased to 65,000 tons. In the postwar period stocks were made available to consumers, and in 1948 the small quantity remaining was transferred to the national stockpile. In 1950, stockpiling was again undertaken to assure that adequate stocks would be available in the event of a major war. The quantity established as an objective was attained, and in March 1964 the scope of the stockpiling program was expanded when the President authorized the establishment of new long-term objectives. By early 1958 the new objective for lead was essentially met, and additional quantities obtained by the Commodity Credit Corporation under barter contracts were scheduled to be added to a supplemental stockpile division of the national stockpile.

Public Law 87–347 enacted on October 3, 1961, provides for subsidy payments to eligible small, domestic producers of lead and zinc ores and concentrates produced on or after January 1,1962, and prior to January 1, 1966. This program provides for payment of 75 percent of the difference between 14.5 cents per pound of contained lead and the average monthly market price for common lead at New York, for the month in which the sale occurred. Payment for zinc is based on 55 percent of the difference between 14.5 cents per pound of contained zinc and the average monthly market prices for prime western zinc at East St. Louis, Ill., for the month in which the sale occurred.

Through September 30, 1964, a total of 128 applications from 13 States had been received of which 62 had been certified and 3 were in process. Total disbursement for lead and zinc through September 1964 under the program was $2.09 million.

Under the Defense Production Act of 1950, as amended, the Defense Minerals Exploration Administration (DMEA) was authorized to grant loans up to 50 percent of approved costs on exploration programs for lead. Public Law 85–701, enacted August 21, 1958, provided the authority for the new Office of Minerals Exploration (OME) which took over the DMEA activities. Through December–June 30, 1962, when lead was removed from the list of eligible metals, DMEA and OME had entered into 289 contracts for exploration of lead (and/or zinc). The total estimated cost was $27.8 million of which the Government's share was $13.9 million. Lead reserves were developed in several areas as a result of the DMEA program. The

program was particularly effective in southern Missouri where important new ore bodies were found which may contain several million tons of recoverable lead and are now being developed.

The International Lead and Zinc Study Group was inaugurated in May 1959 to replace the United Nations Lead and Zinc Committee. Membership was open to governments of countries that were members of the United Nations or appropriate specialized agencies interested in the production or consumption of, or trade in lead and zinc. The Study Group was charged, as an autonomous intergovernmental body, with providing continuous, accurate information on the supply and demand position of lead and zinc and developments in trade on an international basis. The Study Group compiles and publishes monthly statistics on world production and consumption of lead and representatives of the 25 member countries meet annually to review the current situation, review special working group studies of specific problems and evaluate developments and trends in production, consumption, and world trade.

Pursuant to an Escape Clause investigation under authority of the Trade Agreement Extension Act of 1951, the U.S. Tariff Commission in April 1958, found increased imports of lead were causing serious injury to the domestic lead and zinc industry (*18*). On September 22, 1958, the President imposed import quotas on lead and zinc ores, intermediate smelter products and refined lead and zinc metal. The quota effective October 1, 1958, was established at 80 percent of the U.S. average annual import of these materials in 1953–57. The annual quota of 132,890 tons of lead in ores and 221,830 tons of lead metal and bullion was divided on a calendar quarter basis and major exporting countries to the United States assigned a quarterly quota for each category commensurate with imports during the basing period. Minor exporters were included in an "All Other" quota for each category.

PRICES

Lead prices since 1925 have ranged from an average annual low of 3.18 cents per pound, New York, in 1932 (8.32 cents in 1954 dollars) to an average annual high of 18.04 cents in 1948 (19.05 cents in 1954 dollars). During World War II, average sales price plus Government subsidy was about 8.50 cents per pound. Prices advanced markedly after the war and averaged 15.34 cents for 1947–50.

Following the outbreak of war in Korea in June 1950 lead prices attained a high of 17 cents in October. Ceiling prices were established for lead on January 26, 1951, at 17 cents per pound, common lead, New York. On October 2, 1951, the Office of Price Stabilization authorized sales at 19 cents per pound. Increased supplies and lower consumption brought about price reductions in 1952, 1953, and 1954. Early in 1954 consumer demand and a new program of Government stockpiling forced the metal price up to about 16 cents per pound by the end of 1955, at which level it remained until subsequent to April 1957 when cutbacks in consumption and announced cutbacks in stockpiling forced the price to 10¾ cents per pound, f.o.b., New York City on August 13, 1958. During the remainder of 1958 and until November 1, 1961, the price fluctuated between 11 cents and 13 cents per pound. The price decrease from 11 cents to 10½ cents on November 1, 1961, initiated a downward trend to bottom at 9½ cents on February 9, 1962, as heavy stocks and low demand softened the market. On November 1, 1962, an upward trend in price began as stocks decreased under improved industrial consumption and continued through 1963 and 1964 to reach 16 cents per pound on December 10, 1964.

TAXES

The percentage depletion rate for domestic lead mining is 23 percent. Foreign lead mining receives a 15-percent depletion allowance.

TRANSPORTATION

Lead ore containing sufficient lead to permit economic smelting without beneficiation is of small significance. The mined ore is normally concentrated at plants at the mine to minimize transportation expense. Exceptions are custom mills centrally located to serve several small, nearby mines wherein the economics associated with large concentrating plants compensate for the expense of truck haulage of the ore.

The cost of lead concentrate transportation from mill to smelter ranges widely dependent on distance. In 1960, the freight rate from Bonne Terre, Mo., to the nearby Herculaneum smelter was $1.25 per ton of concentrate. At the other extreme, the cost from Adler Creek, Idaho, to the Selby, Calif., smelter was $16.16 per ton. Transportation can thus represent up to 10 percent of the metal value of the concentrate and be a significant factor in cost of production.

Imported concentrates normally require several handlings via rail-boat-rail to the smelter. This transportation cost is a major factor of consideration, along with the other costs of smelting and market price of refined metal, by custom smelters in competitive purchase of foreign concentrates.

RESEARCH

Research is an increasingly important tool of the lead industry. Rising costs of production and marketing and desirability of maintaining a reasonable and stable price have sharpened competition on a world-wide basis and induced both producers and consumers of lead to undertake research projects that promise to yield short or long-term advantage for their products.

The Lead Industries Association founded in 1928 and now comprising some 70 producers and consumers of lead initiated a coordinated program of sponsored research, engineering assistance and information dissemination in the industrial application of lead and its compounds. Affiliated with the American Zinc Institute research program in 1958, the wide geographic scope of industry participation is indicated by the redesignation in May 1963 to the International Lead-Zinc Research Organization (ILZRO).

A significant development in industrial practice was the DM process for continuous casting of lead sheet devised by Broken Hill Associated Smelters and made public through ILZRO. Continuous extrusion of lead alloy cable sheathing is another recent development of importance. Numerous projects sponsored by ILZRO are currently in progress at industrial laboratories, educational institutions, and other facilities (*6*).

Many consumers of lead maintain extensive research facilities to develop new products and improve present products. Anticorrosion paints, vibration cushioning, and sound dampening are a few of the construction areas in which major advance has been made by industrial research, behavior investigation, and experimental application. Electronic research is involved in fabrication and circuitry of lead-compound semiconductors. Storage batteries and gasoline additives are being constantly improved by industry research.

Mining companies have emphasized research in recent years aimed at cost-reducing techniques for exploration, development, mining, and beneficiation. Improvements in trackless haulage, explosives, and automation devices have resulted in improved productivity in mine and mill operations. Technologic advances in geophysical devices have materially assisted exploration for previously hidden mineralization. Smelting procedures are being revised by adoption of the Imperial Smelting Process, to recover zinc metal and lead bullion simultaneously from complex ores.

Research by the Bureau is conducted on new techniques of ore extraction, beneficiation, and refining. Research and investigation directed toward the behavior of rock masses under stress and development of improved ground supports are of major significance. Mine safety research on mobile underground equipment has assisted in utilization of high-productivity equipment. Research in blasting techniques and utilization of nuclear energy in mining are other areas of interest. More effective and economic methods of beneficiating low-grade and complex lead-bearing ores and scrap have received much emphasis in metallurgical research conducted by the Bureau.

The Geological Survey conducts fundamental research relating to the genesis of ore bodies and the mechanics of ore emplacement. From these basic research projects, applied research projects are directed toward defining physical and chemical characteristics of ore bodies that may be used in field investigations of ore potential (*17*).

OUTLOOK

The two major outlets for lead are in storage batteries and gasoline additives which together account for over 50 percent of the total consumption of lead in the United States. Demand in these applications will grow in proportion to the number of cars on the road and the distance traveled. Since 1959 this combined use of lead in the United States has followed the 3.6 percent growth rate of GNP, and as these uses do not appear likely to suffer from technological substitution the growth is expected to continue.

Consumption of lead in the other combined historic uses chiefly in metal products and pigments, has shown a decline of less than 1 percent annually since 1959. Increases in some applications have been counterbalanced by declines in other fields. Intensified research in applications in the construction area are expected, however, to provide a modest growth element. The growth rate of lead consumption for all uses, amounting to about 1.75 percent since 1959, is thus expected to increase by about 2 percent annually to about 1.3 million tons by 1970.

Domestic mine production is expected to increase substantially under improved demand from expansion at presently producing mines and, chiefly, from new facilities presently planned, especially in Missouri. Domestic production is expected to achieve 400,000 tons annually by 1970.

Secondary lead recovered from scrap is governed by the recycling of scrap, over one-half

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of which is contributed by wornout storage batteries. A moderate growth of 1.5 percent annually is envisioned to 525,000 tons by 1970 as this supply increases and price continues to remain attractive to scrap collectors.

The United States will continue to require about one-third of its total lead supply from foreign sources. Continuing high-level demand under presently limited imports and time requirements to develop domestic supply could result in a short-term, tight supply in the United States with resulting market disruption. World reserves of lead are adequate and indicated development of additional foreign supply sources, especially in Canada and Ireland, will provide a substantially larger output potential. The new developments both domestic and foreign along with presently operating mines and smelters are, however, expected to provide an ample long-term world supply of lead at a competitive price with the other metals.

PROBLEMS

The basic problem of the lead industry in past years has been the coordination of domestic and free world mine and smelter production to achieve a closer balance with consumption. This problem has many facets—mineralogical, industrial, geographical, and geopolitical. The coproduct association of lead and zinc in ore deposits, particularly in the Western United States and foreign countries, wide variations in grade-of-ore and production costs, general geographic separation of producing and consuming areas, and nationalistic as well as unstable political climate existing in some producing countries—all contribute to periodic surpluses and shortages in supply in comparison to demand.

The domestic mining industry is faced with a need to determine the nature and quantity of reserves and potential resources and to develop more efficient techniques and equipment for exploitation of the available ore deposits in competition with foreign suppliers.

A problem facing domestic smelters, and one that will probably become more serious in the future, is the maintenance of or establishment of a dependable and economic supply of primary raw material for existing plants in competition with foreign smelters. The nationalistic trend toward refining in the country of origin of the ores will diminish availability of ores for export and refining elsewhere.

The lead industry is influenced predominately by gasoline powered transportation as storage batteries and as gasoline additives. A continuing problem exists in the maintenance of lead superiority in these fields by research and technologic improvement and, also, in the other historic uses of lead constantly vulnerable to substitution by competitive materials. A need exists to determine and to develop other potential and advantageous applications of lead in construction and allied industrial fields.

Problems exist in many areas of utilization. The temperature requirements for lead-based solders, especially in automobile radiators, are increasing and improved mechanical properties and corrosion resistance at these elevated temperatures is needed. Difficulties are encountered in obtaining a strong bond and an impervious coating in using lead to clad other metals. Existing methods of joining lead pipe and cable are expensive and inefficient, and high-pressure lead calking methods require improvement for modern use. A number of lead compounds have properties peculiarly suited to use in protective and decorative coatings; however, the lead industry's growth in this area has not paralleled the growth of the coatings industry. Toxicity to humans is a problem of continuing concern and research study, especially in the area of atmospheric pollution control of highway and industrial plant fume.

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LIGNITE

By Eugene T. Sheridan [1]

LIGNITE is a soft and porous carbonaceous material that is the intermediate stage between peat and subbituminous coal. Lignite is brownish-black in color and is referred to sometimes as brown coal.

There are known deposits of lignite in 15 States, and recoverable reserves have been estimated at 224 billion short tons. The bulk of the reserves occur in central and western North Dakota, northwestern South Dakota, and eastern Montana. There are also important deposits in Texas.

The lignite industry is concentrated in North Dakota which had 30 of the 35 active mines and about 90 percent of the total production in 1963. Virtually all of the remaining output was produced in Montana. Lignite in both States is restricted for the most part to local areas of production where it is used principally for electric-power generation and residential and industrial heating.

World production of lignite for 1963 was estimated at 760 million short tons. East Germany was the largest producer, followed by the U.S.S.R. and West Germany.

BACKGROUND

Lignite was used as domestic fuel in local areas from the time of settlement, but the lignite industry was not established until the latter part of the 19th century when mines were reported operating in California, Montana, North Dakota, South Dakota, and Texas. Data on production before 1930 are incomplete, but the U.S. Geological Survey reported in its annual report of the mineral resources of the United States for 1900 that production in North Dakota and Texas, the leading producing States at this time, totaled 382,795 tons.

The industry in Texas climbed from an annual output of 252,912 tons in 1900 to 1.4 million tons in 1914, then averaged about 1 million tons per year for the next two decades. Production began to decline in the late 1930's, however, as natural gas and petroleum took over fuel markets held by lignite, and by 1950, less than 20,000 tons of lignite was produced in Texas annually. Currently, lignite is mined at Rockdale in Milam County and at Darco, Harrison County. It is used principally for generating electric power, as a source of activated carbon, and as an oil well drilling-mud additive.

Production in California in 1900 was reported to be about 70,000 tons. California reserves are small and restricted to one area, and lignite has not been able to compete successfully as a fuel in this State. Only one mine is known to have been in operation in California in the past decade and the output from this mine has been processed for the recovery of montan wax.

Although still relatively small, the industry in Montana has expanded within the past decade with the use of lignite as fuel for generating electric power. From an output of only 25,572 tons in 1957 when virtually all was used for space heating, production increased to 289,532 tons in 1963. One power-generating plant in eastern Montana presently is using lignite for fuel.

Virtually all lignite produced in South Dakota is used for domestic fuel. The industry in this State has always been small and annual output has never exceeded 100,000 tons. Production in 1963 was only 16,561 tons.

Output in North Dakota, the leading producer since the 1920's, increased from 1.3 million tons in 1925 to 3.3 million tons in 1950, then gradually decreased to 2.3 million tons in 1958. Production since then has remained roughly at this level. North Dakota's lignite reserves are huge, and lignite always has been the major fuel used within the State. The industry has

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been restricted in development, however, because the low calorific value and high moisture content of lignite confine its use to a relatively small marketing area. Most of the lignite produced in North Dakota is used for residential and industrial heating, and for electric-power generation.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Compared with the bituminous coal industry where active mines exceed 8,000, the lignite-mining industry is small; only 35 mines in 3 States were active in 1963. This number does not include mines with production of less than 1,000 tons, nor does it include the two active operations in Texas. Most of the industry is concentrated in North Dakota, which had 30 of the 35 active mining operations in 1963. Montana had four active mines and South Dakota had one.

The size of operations varied greatly, but most were small, with tonnages of less than 50,000 tons. Of the 30 mines operating in North Dakota in 1963, only 6 had outputs ranging between 100,000 and 500,000 tons, and only 1 had an output that exceeded 500,000 tons. Of Montana's four active operations, only one produced more than 50,000 tons in 1963.

The relative size of lignite mines in the United States in 1963 is shown in table 1.

TABLE 1.—*Relative size of lignite mines in the United States in 1963* [1]

Size	Number of plants	Production (short tons)
Under 50,000 tons	26	246,853
50,000–99,999 tons	1	58,172
100,000–199,999 tons	3	495,764
200,000–500,000 tons	4	1,192,366
Over 500,000 tons	1	711,926
Total	35	2,705,081

[1] Mines with production over 1,000 tons but exclusive of Texas.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Coals are separated into four general classes according to rank or degree of coalification—(1) Anthracite, (2) bituminous, (3) subbituminous, and (4) lignite.

The great variation in the composition of coals can be seen from the following analyses, on an ash-free basis, of a typical lignite and an anthracite:

	Lignite (percent)	*Anthracite (percent)*
Fixed carbon	33	92
Volatile matter	26	5
Moisture	41	3
Total	100	100

For the higher rank coals, rank is determined by the amount of fixed carbon and volatile matter in the coal as determined by proximate analysis. For lower rank coals, heating value and agglomerating properties denote rank. Lignite is our lowest rank of coal and, according to the American Society for Testing Materials (ASTM) classification, all coals with a calorific value of less than 8,300 B.t.u. per pound (moist, mineral-matter-free basis) are termed lignite. The class lignite is subdivided into two groups—Lignite A, which includes coals with calorific values between 6,300 and 8,300 B.t.u. per pound, and lignite B, which denotes coals with heating values of less than 6,300 B.t.u. per pound.

Most of the lignite reserves of the United States fall into the "A" grouping, and all lignite presently produced is of this type. Lignite B is similar to most of the brown coals that occur in Germany and other European countries.

As lignite production in the United States is relatively small and virtually all is used locally for heating and electric-power generation, lignite is not sold by grades and specifications, except that it is sold to powerplants on the basis of calorific value and ash and moisture content. It usually is subjected also to freezeproofing methods prior to shipment.

Although a standard size classification system has not been adopted by the industry, lignite is sold by certain designated sizes in common use, as shown in table 2. Generally speaking, lignite, as mined, that passes through a 2-inch mesh or smaller screen is called screenings or industrial size. To this may be added a 2-inch or smaller top size produced in the crushing and screening of other sizes. Stoker size prepared by crushing lump lignite is designated by the word "crushed" as it has a more uniform size distribution than the regular screened size. Nut sizes of 2 by 1 inch, or 2 by 1½ inches, may be screened from the crushed product. Large-size double-screened coals used in domestic heating and cooking equipment are described by their use, as plus 8- or plus 6-inch lump, or 8- by 4-inch furnace size.

Leonardite, a coal-like substance associated with lignitic outcrops, is thought to be derived from lignite by the process of natural oxidation. The significant difference between leonardite and lignite is the oxygen content; leonardite contains 28 to 29 percent oxygen and lignite, 19 to 20 percent. Leonardite is little known out-

side lignite-producing areas and deposits have been developed commercially only to a minor extent.

TABLE 2.—*Common designation for lignite sizes, as produced*

Designation	Size (inches)
Lump	plus 8
	plus 6
Furnace	8 by 4
	6 by 3
Stove	4 by 2
	3 by 2
Nut	2 by 1
	2 by 1½
Stoker, crushed	2 by 0
Industrial or screenings	2 by 0
Industrial stoker or rescreened screenings	2 by ¼ or 1¼ by ¼

TECHNOLOGY

Geology

Although coal commonly is thought of as a mineral, it differs from minerals, such as stone and iron ore, in that it is of organic origin. Coal was formed from the remains of living vegetation—trees, shrubs, roots, herbs, and vines—that grew many millions of years ago in swamps and bogs. Century after century, the dead vegetation accumulated to a gradually increasing depth, and only after a series of transformations, usually by movements of the earth's crust accompanied by heat and pressure, these deposits were gradually converted to coal. Varieties of coal, which represent different degrees of conversion, are known as ranks. Anthracite, which represents the greatest degree of conversion, is the highest rank of coal; lignite is the lowest.

Peat is the initial stage in the formation of lignite and other coals. When plant materials fall upon dry ground, they are attacked by fungi and bacteria and decompose rapidly. However, when the plant material falls into water or on soil saturated with moisture, atmospheric oxygen, which controls bacterial activity, is excluded and decomposition is retarded. Plant debris accumulated under such conditions results in the formation of peat, and an accumulation of many layers of plant materials forms a peat deposit.

The changes involved in the conversion of peat into coal are not completely known, but it is thought that the transformation is due largely to pressures exerted by overlying strata laid down on a peat deposit, and by mountain building and earth disturbances. Changes in elevation are constantly occurring in the earth's crust, and the subsidence of a peat deposit followed by an accumulation of overburden appears to have been the initial change. In the course of time subsidence of the surface may have been reversed and the deposit elevated, sometimes above its original level, to form one of the convolutions of strata of hills or mountains. The combination of heat and pressure accompanying such a movement plus the continued exertion of these forces over very long periods, greatly altered the chemical and physical properties of the original plant structures, and the resulting material, which varies in degree of transformation, is called coal.

Coalification is extremely slow when it depends mainly upon pressure generated by overlying rock. For this reason many coal deposits are still of low rank, that is, in an early stage of coalification, although they may have been buried millions of years. The advanced state of coalification typified by Pennsylvania anthracite probably is due to the enormous pressures to which deposits were subjected when the Appalachian mountains were formed. The anthracite seams are thought to be extensions of the bituminous seams of central and western Pennsylvania that were subjected to greater pressures and temperatures during the mountain-building era.

Seams or bands of coal, separated by layers of clay, shale, and other organic material, apparently represent the effects of alternate depressions and elevations during which succeeding layers of peat were formed. Inorganic materials within the coal probably were deposited as suspended particles in the water in which the peat was formed, or may have evolved from the organic materials of the coal itself.

Mining, Preparation, and Storage

Virtually all lignite is produced by strip mining, but most stripping operations are small and production is concentrated at a relatively small number of large operations. Of the 31 strip mines active in 1963, 8 produced almost 90 percent of the total output of the industry. There were only four active underground mines in 1963, and their combined production was less than 1 percent of the total lignite output.

One factor of major importance in a stripping operation is the thickness of the overburden in relation to the thickness of the seam being mined. Individual beds of lignite vary substantially in thickness, ranging from about 3 feet to 25 feet. The depth of overburden also varies, and in some instances it is necessary to remove overburden up to 70 feet thick and place it in a position where it will not interfere with subsequent operations. Overburden in the lignite areas, however, usually is composed of unconsolidated clays with occasional shale or

sandstone, which can easily be removed by stripping shovels, draglines, or bulldozers.

Lignite operations generally employ about the same stripping methods as bituminous coal stripping mines. Stripping consists of removing the overburden in successive uniform cuts and placing it in a previous adjacent cut from which lignite has been removed. The equipment used depends chiefly upon the depth of the overburden and the financial resources of the producing company.

A newly designed strip-mining machine called a wheel excavator was being installed in 1964 at Truax-Traer Coal Co.'s Glenharold mine in North Dakota. This machine has an expected advantage over conventional equipment in that it will provide for the simultaneous mining of four beds of lignite. The discharge end of the machine can be manipulated in a 105° arc. When refuse is being mined, the discharge boom is over the spoil pile; when lignite is being mined, the discharge boom is rotated to a stockpile in the pit.

Preparation processes in the lignite industry consist principally of crushing and screening, and in some instances, treating with oil to improve handling characteristics by reducing dust, and freezeproofing. Other processes common to the coal industry, such as mechanical cleaning or washing, are not practiced with lignite because ash content usually is low, and lignite is unresponsive to such forms of beneficiation. Lignite as shipped generally has an ash content of 5 to 8 percent. Removing the weathered layer on top of the uncovered bed before loading and leaving the bottom of the bed for the loading shovel reduce the inclusion of extraneous matter, and quality for a given mine is quite uniform. In general, the mineral matter of lignite is largely composed of finely divided particles that are difficult to separate.

As the market for lignite is largely for stoker and industrial sizes for power generation, most lignite is crushed and, at the larger mines, is passed through a primary breaker, then over a shaker screen where the various lump sizes are separated for sale or additional crushing. Double-roll crushers are used for secondary crushing in many instances, but other types of equipment such as hammermills also are used for size reduction.

Lignite normally is not dried prior to shipment, but a few large companies dry a small portion of their production and mix it with natural lignite for freezeproofing purposes. One method used is pneumatic or entrained drying, which is applicable only to fine materials. In this process moisture is removed from fine-sized lignite suspended in a cyclone separator by a rapidly moving stream of hot gases. The equipment includes a heat source such as a firebox and stoker, a duct into which the lignite is dispersed in the hot gas stream, a cyclone separator equipped with an air lock, and an exhauster which pulls the gases and fine solids through the system.

In steam drying, which has been used commercially in Europe, lignite is placed in an autoclave and heated with saturated steam at from 250 to 400 pounds per square inch, gage. During a period of heating, followed by a period of steaming under pressure, some of the moisture in the lignite is expelled and drained off as liquid water. The residual heat in the lignite causes additional moisture to be removed during the pressure-release period. Since part of the water is removed as a liquid, the thermal requirement for steam drying per unit quantity of moisture removed is less than for processes in which all moisture is removed by vaporization.

Lignite must be stored under strict storage procedures to avoid spontaneous combustion and slacking, or degradation of the product. Where the amounts stored are small and removal is continuous, lignite is stored in bins or silos. If stored for long periods, airtight covers must be used on the bins or silos. For large tonnages, lignite usually is stored in compacted piles according to special stockpiling procedures. These usually consist of constructing the piles in layers, 1 foot or less in thickness, and crushing, leveling, and compacting each layer with rollers.

Combustion

Lignite can be burned at heat-release rates and efficiencies nearly comparable to those of higher rank coals, and large quantities are consumed each year in firing boilers for electric-power generation. Because of its high moisture content, however, the heating value of a pound of lignite is only about one-half that of many eastern coals. Therefore, when lignite is burned for power generation, the fuel-handling and preparation equipment must be increased proportionately in size, and the power required for operating this equipment must be increased accordingly. Boiler efficiencies also are about 5 percent less than those of boilers burning other fuels because of the heat required for moisture evaporation. To obtain maximum efficiency, lignite furnaces generally are built higher and have somewhat greater volume per unit capacity than furnaces burning higher rank fuels.

As with bituminous coal, lignite can be burned successfully in powerplant boilers using underfeed stokers, traveling-grate stokers, spreader stokers, pulverized burning equipment, and cyclone burners. The first really successful

equipment suitable for lignite was the forced-draft, traveling-grate stoker, which was used extensively for a number of years until it was replaced by the more efficient spreader stoker. Spreader stokers used in conjunction with traveling grates are used at most of the smaller plants, but larger installations use the unit-pulverizer method of firing because spreader stokers have boiler-size limitations.

The most recent development in coal-burning equipment is the cyclone burner, which was developed to obtain higher efficiencies and improved performance in burning high-ash coals with low-ash fusion temperatures. This burner has a refractory-lined, water-cooled, combustion chamber into which pulverized coal and air are introduced tangentially at one end so that the air and fuel are given a whirling motion. The fuel is burned at high temperatures as it travels through the burner, leaving most of the molten ash adhering to the cylinder wall, from which it flows by gravity to a slag tank. As with any unit designed for liquid ash removal, this furnace must operate well above the fusion temperature of the ash for satisfactory tapping of the slag.

Carbonization

Carbonization is the thermal processing of coal in ovens or retorts in the absence of air. Such processing yields a liquid fraction containing tar and other basic chemicals; a relatively low B.t.u. gas; and a solid residue called char or coke. Carbonization of lignite in the United States has been limited because the carbonization products are different from those of bituminous coal and are in small demand. Lignite, when carbonized, forms a char rather than coke and is not satisfactory for metallurgical applications. The small quantity of char currently produced is used principally for manufacturing briquets.

In the briquet plant at Dickinson, N. Dak., of the Husky Oil Co. of Cody, Wyo., lignite is crushed to 4 inches or less and carbonized in Lurgi-Spülgas retorts. After carbonization, the char residue settles at the bottom of the retort where it is cooled by recycled carbonization gas and discharged. A gas mixture containing tars and other products of combustion is drawn off at the top of the carbonizer and, after processing for the removal of dust and tars, the gas is recycled to the carbonizer to supply heat for the process. The tars and light oils, after separation from the water condensate, are distilled into a liquid fraction and a pitch residue. The distillate is used as a wood preservative, and the pitch, supplemented by petroleum asphalt, as a binder for manufacturing briquets suitable for residential heating.

The Husky briquetting plant also manufactures a smokeless barbecue briquet. In this process, sulfur-laden pyrites are removed from the char, which then is mixed with a starch binder and compacted at 5,000 to 10,000 pounds per square inch. After drying to 4 percent moisture, the briquets are cooled for 72 hours, packaged in small bags, and sold as fuel for barbecue grills, ovens, and broilers.

Gasification and Hydrogenation

The gasification products of lignite generally are defined as synthesis gas and producer gas. Producer gas is made by blowing air through a solid-fuel bed with or without the addition of steam. The resulting product is a relatively inexpensive gas containing a high percentage of nitrogen. Because of its low heating value, producer gas is not suitable for utility distribution and normally is used at or near the point of production. Gasification of lignite or brown coal is done on a commercial basis in several foreign countries, but lignite is not processed in this manner in the United States.

Lignite can be converted also into liquid products having potential use as chemicals or fuel by a process called hydrogenation. This is a type of processing in which the complex compounds of the coal are split and partially broken down into lower molecular weight products by the direct addition of hydrogen under pressure.

USES

Lignite is used in the United States principally as fuel for residential and industrial heating and for generating electric power. Approximately two-thirds of the total consumed in 1963 was used in powerplants, and most of the remainder, for space heating. Small quantities were used for several other purposes.

One plant carbonized lignite in a Lurgi gasifier and produced a char which was then briquetted. This plant produced two types of briquets: (1) a conventional fuel briquet that was sold for space heating, and (2) a smokeless briquet that was sold as fuel for outdoor grills.

Some lignite deposits yield montan wax and the output of a small mine at Ione, Calif., is operated for this purpose. Wax is recovered by a solvent-extraction process and used in polishes, phonograph records, candles, carbon paper, and crayons.

Lignite can be used as a source of activated carbons, and one plant in Texas processes lignite for this purpose. Activated carbons derived from lignite are used for decolorizing solutions, water treatment, recovery of solvents, gas absorption, recovery of gold, and extraction of iodine.

Leonardite, a form of oxidized lignite, is used as a dispersant, for viscosity control in oil-well drilling muds, as a stabilizer for iron-exchange resins in water treatment, and as a source of water-soluble brown stain for wood finishing. Leonardite is also a source of humic acids and a plant in Wyoming has been reported to be producing limited quantities of lignite-based fertilizer having a humic-acid content of 50 percent.

Lignite is used also in a number of foreign countries as a primary raw material for the production of chemicals, heating gases, and liquid fuels.

RESERVES

The potential recoverable reserves of lignite in the United States are estimated to total 224 billion short tons, approximately one-quarter of the total reserve of all ranks on a tonnage basis. However, the calorific value of lignite is lower than that of other coals, and, on the basis of equivalent heating values, the lignite reserve represents about one-sixth of our total coal resource.

Lignite occurs in three general areas—The northern Great Plains, the gulf, and the Pacific coast. The northern Great Plains region includes the western half of North Dakota, eastern Montana, northeastern Wyoming, and northwestern South Dakota. Deposits in this region are in extensive blanket-like beds, and the recoverable reserve is estimated at 220 billion tons, about 98 percent of the U.S. total. North Dakota has the most extensive deposits, with recoverable reserves estimated to total 175 billion tons, nearly four-fifths of the U.S. total.

Gulf region deposits, which are in the lower Mississippi Valley, occur in Alabama, Arkansas, Kansas, Louisiana, Oklahoma, and Texas. The principal deposits in this region are in Texas where the recoverable reserve is estimated to be 3.4 billion tons, somewhat less than 2 percent of the U.S. total.

Reserves of the Pacific coast are in the central and western parts of California and in the western parts of Oregon and Washington. There are also small deposits of lignite in Idaho and Nevada. Unlike the extensive blanket-like beds of the northern plains, these deposits, as those of the gulf region, are discontinuous and relatively small. Reserves in these States constitute less than 1 percent of the total lignite resource of the United States.

Table 3 shows the geographic distribution of reserves, and table 4 shows lignite reserves in relation to reserves of all other ranks of coal.

TABLE 3.—*Potential recoverable reserves of lignite [1] by States, as of Jan. 1, 1964*

State	Million short tons
North Dakota	175,352
Montana	43,766
Texas	3,440
South Dakota	1,017
Arkansas	175
Alabama	10
Other States [2]	25
Total	223,785

[1] Estimated on the basis of 50-percent recovery of the total estimated reserve.
[2] Includes Alaska, California, Idaho, Kansas, Louisiana, Nevada, Oklahoma, Washington, and Wyoming.

TABLE 4.—*Potential recoverable reserves of various ranks of coal,[1] based on bituminous coal equivalent, as of Jan. 1, 1964*

	Million short tons	Equivalent million short tons of bituminous coal [2]	Percent of total coal reserves on B.t.u. basis	Calorific values used for conversion (B.t.u.'s)
Anthracite	8,000	8,000	1	12,700
Bituminous	378,000	378,000	57	13,100
Subbituminous	218,000	158,000	24	9,500
Lignite	224,000	115,000	18	6,700
Total	828,000	659,000	100	

[1] Estimated on the basis of 50-percent recovery of the total estimated reserve.
[2] Based upon a calorific value of 13,100 B.t.u. per pound.

SOURCES OF STATISTICAL INFORMATION

The sources of data on lignite are the same as those outlined for coal in the annual chapter on bituminous coal in the Bureau of Mines Minerals Yearbook, volume II. Most of the statistical information was based upon detailed annual reports of production, mine operations, and product distribution, furnished by producers to the Bureau. For production not reported to the Bureau (chiefly that of small mines), data were obtained from various State mine departments and, in a few instances, from railroad carloadings. Thus, complete coverage of all mines producing 1,000 tons or more per year was included in this report.

PRODUCTION AND CONSUMPTION

Production of lignite in the United States in 1963 was 2.7 million tons. This quantity does not include the production of lignite by two companies in Texas, for which data are confidential, nor the production of mines with an output of less than 1,000 tons. North Dakota

was the largest producer, with about nine-tenths of the total output. Montana produced virtually all of the remainder, but one mine in South Dakota produced 17,000 tons.

Production in North Dakota was centered in Mercer County in the west-central part of the State, and in Burke and Ward Counties in the northwest. The largest producers were the Truax-Traer Coal Co., the Knife River Coal Mining Co., and Baukol-Noonan, Inc. Montana's output was produced principally in Richland County in the northeastern section of the State. The Knife River Coal Mining Co. is the principal producer of lignite in Montana.

Virtually all lignite was produced by strip mining. Except for a small decrease in 1963, caused principally by the relocation of one large operation and the adoption of more selective mining practices at others, lignite production has increased moderately each year since 1958. Compared with average production for 1957–59, output in 1963 increased 6 percent.

World production of lignite for 1963 was estimated to total 796 million tons. U.S. production was less than 1 percent of the world total.

Lignite production in the United States, by States and counties, in 1963, is shown in table 5.

TABLE 5.—*Lignite production in the United States in 1963* [1]

State and county	Number of mines	Production (short tons)
Montana:		
Powder River	1	(2)
Richland	2	(2)
Sheridan	1	2,653
Undistributed		286,879
Total	4	289,532
North Dakota:		
Adams	1	27,236
Bowman	1	(2)
Burke	2	(2)
Burleigh	1	9,994
Divide	1	(2)
Dunn	1	3,714
Grant	4	19,590
Hettiger	1	3,487
McClean	3	61,299
Mercer	3	1,042,578
Morton	3	12,784
Oliver	2	7,623
Stark	3	(2)
Ward	3	(2)
Williams	1	1,880
Undistributed		1,208,803
Total	30	2,398,988
South Dakota: Dewey	1	16,561
Grand total	35	2,705,081

[1] Mines with production over 1,000 tons but exclusive of Texas.
[2] Included with "Undistributed."

Consumption of lignite in 1963, as shown in table 6, was 2.6 million tons. Of this quantity, consumption by powerplants, according to data compiled by the National Coal Association from records of the Federal Power Commission, was 1.7 million tons, nearly two-thirds of the total lignite used by utilities and shipped by producers to other consumers. Of the total used for electric-power generation, 58 percent was consumed at plants in North Dakota and South Dakota, and 24 percent in Minnesota. These three States also used a combined total of nearly 1 million tons of lignite for heating purposes.

TABLE 6.—*Consumption by electric utilities, and shipments by producers to retail dealers and other consumers, of lignite in the United States in 1963*

[Short tons]

State	Utility plants [1]	Retail dealers [2]	All other uses [2]	Total
Minnesota	406,000	6,000	241,000	653,000
North Dakota and South Dakota	963,000	407,000	299,000	1,669,000
Montana and Wyoming [3]	304,000	----------	6,000	310,000
Total	1,673,000	413,000	546,000	2,632,000

[1] Based on data compiled by the National Coal Association from records of the Federal Power Commission.
[2] Shipments of lignite as reported by producers to the Bureau of Mines.
[3] Does not include Texas.

PRICES

The average value per ton of all lignite produced in the United States in 1963, f.o.b. plant, was $2.17. Prices of lignite have steadily decreased as a result of increased productivity, and the average price was $0.15 per ton less than that in 1957–59. An indication of the relative costs of producing lignite by strip mining and underground mining is shown in table 7. The average value per ton of all lignite produced at underground mines in 1963 was $4.63, compared with only $2.17 for lignite at strip mines.

TABLE 7.—*Summary of data on lignite mines in the United States operating in 1963* [1]

	Underground	Strip	Total
Number of mines	4	31	35
Production ---------- short tons	7,048	2,698,033	2,705,081
Average value per ton	$4.63	$2.17	$2.17
Average number of men working daily	12	332	344
Average number of days worked	113	209	206
Number of man-days worked	1,360	69,350	70,710
Average tons per man per day	5.18	38.90	38.26

[1] Mines with production over 1,000 tons but exclusive of lignite produced in Texas.

EMPLOYMENT AND PRODUCTIVITY

Employment at lignite mines has declined steadily because of increased mechanization and the continued change from underground to strip-mining operations. Compared with 1957–59 when the average number of men working daily was 384, there was an average of 344 men

employed by the industry in 1963. Of this number, 12 were employed at 4 underground mines and 332 at 31 strip mines. Peak employment was in 1939 when a total of 2,130 men were employed at lignite mines.

Productivity during the past decade, as measured in tons of output per man-day, has ranged from a low of 32.68 tons in 1956 to a high of 42.46 tons in 1962. The trend was steadily upward from 1958 until 1963 when output decreased because of more selective mining practices at some stripping operations and the movement of one large strip mine to another location. Productivity at strip mines far exceeded that of underground mines; output at stripping operations in 1963 was 38.9 tons per man-day, compared with only 5.18 tons per man-day for underground operations.

Statistical data on employment and productivity are shown in tables 7 and 8.

TABLE 8.—*Production, value, men working daily, days active, man-days, and output per man per day at lignite mines in the United States* [1]

Year	Production (short tons)			Average value per ton f.o.b. mines	Average number of men working daily	Average number of days worked	Number of man-days worked	Average tons per man per day
	Underground	Strip	Total					
1957–59 (average)	18,550	2,535,421	2,553,971	$2.32	384	197	75,471	33.83
1960	13,669	2,732,399	2,746,068	2.29	384	197	75,662	36.29
1961	12,077	3,005,442	3,017,519	2.24	367	202	73,966	40.80
1962	10,089	3,045,175	3,055,264	2.23	354	203	71,952	42.46
1963	7,048	2,698,033	2,705,081	2.17	344	206	70,710	38.26

[1] Excludes lignite produced in Texas.

RESEARCH

Although the use of lignite in the United States is relatively small, the potential of the resource has tremendous magnitude, and a large amount of effort has been devoted to the improvement of technology relative to using lignite as a fuel and as a source of raw materials for the production of gas and chemicals, and to the development of new product uses. Because of the small size of the industry, much of the research has been conducted by the Federal Government, principally the Department of the Interior through the Bureau of Mines. Industry, however, has become increasingly aware of the fruits of research and is expending effort along these lines, contracting for most of the work with commercial laboratories. In implementing its responsibilities for conserving and developing the Nation's mineral-fuel resources, the Bureau of Mines has conducted a large-scale research program on lignite for many years at its Lignite Research Laboratory at Grand Forks, N. Dak. Investigative studies have been widespread, ranging from fundamental and basic research to applied research and development. Current work has been concerned principally with the use of lignite as fuel in steam-generating units and as a solid reductant for iron ore; storage techniques; burning characteristics; preparation, pulverizing characteristics, and pneumatic drying; extraction of humic acids; and the hydrocracking of low-temperature lignite tar.

Emphasis has been placed on the upgrading of lignite for fuel. Because the use of lignite has been somewhat limited by its inherently high moisture content, methods have been developed for removing some of the moisture, particularly to keep it from freezing when shipped. Relatively recent studies by the Bureau have shown that the addition of 15 percent by weight of dried lignite fines to as-mined lignite before shipment is superior to the conventional oil-treatment method of freezeproofing, a nd one large producer has adopted this process for all lignite shipments. Another producer partially dries all of his product as a method of freezeproofing.

Another area of study is carbonization. In addition to char, the carbonization of lignite results in the production of tar and other chemical materials that normally must be sold to carbonize lignite economically. The Bureau has devoted substantial attention to the characterization of such products with the view of developing methods for upgrading so that these products can be sold in established markets.

The production of gas by total gasification procedures offers the potential for a large tonnage outlet for lignite, and the Bureau has made numerous investigations in this area. Synthesis gas consists chiefly of carbon monoxide and hydrogen, chemicals which after suitable purification and modification, can be used for the production of ammonia, synthetic liquid fuels, and various organic chemicals. Synthesis gas also can be burned as a reducing gas in metallurgical applications. Experiments on fixed-bed gasification are being continued by the Bureau, and a pilot-scale slagging gasification plant for evaluating the German Lurgi process has been erected at the Grand Forks Laboratory.

OUTLOOK

The short-range future for lignite appears to be one of moderately increased production with the bulk of the output being consumed in present markets, namely residential and industrial heating and electric-power generation. An increase in production, however, will result principally from an increased demand for powerplant fuel because heating markets that have been lost to oil and gas probably will not be recaptured. The inroads made by oil and gas into lignite heating markets in recent years appear to have reached a peak, and the lignite industry should be able to retain present heating markets. New discoveries of natural gas, however, could present another threat. It is expected that lignite will continue as the principal fuel of electric-utility plants in lignite-producing areas and that electric power requirements in the next few years will increase at a rate more or less consistent with population growth. Further expansion of utilities will be tied to the expansion of existing local industries or the establishment of new ones.

The long-range future for lignite is more difficult to forecast. Fuel and energy markets undoubtedly will continue to increase, but the extent of the increase will depend upon technological developments and other factors, such as the attraction of new industries to the lignite-producing areas, or the development of new product uses. Fuel marketing areas probably will be extended in the future, by removing moisture from the lignite and shipping an upgraded product. There is also the possibility of onsite powerplants producing electric power for long-distance transmission.

Markets for barbecue briquets made from lignite char should continue to expand, and leonardite should find increased usage as a conditioning agent for oil-well drilling muds. The key to lignite development, however, will be the establishment of new use markets that will consume large tonnages. Markets that appear to show the most promise would use lignite as a raw material for the production of chemicals or synthesis gas, as a fuel for the production of prereduced taconite pellets, or as a source of humic acids for the preparation of fertilizers.

PROBLEMS

The lignite industry has been limited in expansion by a number of interrelated factors, but the principal limiting factor is the nature of the product. Being a low-rank fuel with a high moisture content, lignite can compete with other higher rank fuels only in local fuel markets because transportation costs restrict its movement. The present marketing area for lignite extends about 300 miles east and southeast from the areas of production. The eastern market extends to the area where the price of lignite is equaled by that of eastern coals delivered at northern Lake ports; the southeastern market extends to where prices are equal to those of coal barged up the Mississippi River. North and west of the lignite deposits, markets are limited by the lack of population and the availability of higher-rank coals. The marketing area for lignite, therefore, is very small. But this disadvantage is compounded by the small population and limited industrial markets within the area where lignite is competitive.

A major problem encountered in burning lignite in power stations is boiler fouling. This is a condition that occurs when deposits of ash form on the convection surfaces of boilers, gradually decreasing efficiency to the point where the boilers must be taken out of service for manual cleaning. Although the problem is complex and not fully understood, it is suspected that some of the causes of fouling are due, not only to impurities in the lignite, but also to compounds appearing in the ash. Some of the problems of ash deposition can be solved by using a suitable boiler design and modern cleaning devices. More information is needed, however, on the various impurities in lignite ash, such as alkalies, that are thought to be responsible for fouling, and the relationship between certain other factors, such as ash particle size and exit-gas temperatures, that are associated with ash deposition.

A continuing problem of the industry is storage. Lignite "weathers" or "slacks" badly upon drying, and lump sizes deteriorate when lignite is stockpiled. It is subject also to spontaneous heating and can be stored only under controlled conditions.

Because of its high moisture content, lignite becomes severely agglomerated when shipped in cold weather, and unloading railroad cars containing frozen lignite presents a serious problem. A number of freezeproofing methods have been developed, however, and the problem usually is eliminated if lignite is processed prior to shipment.

The industry is hampered by the lack of detailed information on specific lignite deposits. Data on the size and extent of reserves in in-

dividual deposits are very limited, and only meager information is available on seams and the impurities that exist in various seams and strata. The development of such basic information on reserves would, undoubtedly, promote a more extensive utilization of lignite resources.

Another basic problem is that most lignite-producing companies are of relatively small size and have a limited capacity for individual research and engineering. The lignite industry is very cognizant of its problems, however, and actively participates in the work of the Lignite Advisory Committee, a group appointed by the Secretary of the Interior in 1960 to consider current problems of the lignite industry as an aid in the programing of research.

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LIME AND CALCIUM

By Perry G. Cotter [1]

CALCINATION of limestone, marble, chalk, calcareous marl, shell, and dolomite at moderately high temperatures releases carbon dioxide gas and leaves behind a solid residue of quicklime, which is usually calcium oxide but may be calcium-magnesium oxide as well. Addition of water to quicklime causes rapid hydration to calcium hydroxide, $Ca(OH)_2$, or hydrated lime.

Manufacture and use of quicklime and hydrated lime is almost as old as recorded history, and the importance of these commonplace, time-tested, construction and chemical materials has not diminished at all. More quicklime and hydrated lime than ever before is required to satisfy the growing needs of modern civilization. To the few, original, primary uses in building and agriculture have been added thousands of chemical and industrial uses in modern times. Most quicklime and hydrated lime enter into chemical and industrial applications. Smaller quantities are employed in construction in mortar and plaster and in soil stabilization and in agriculture as a soil neutralizer and conditioner. Being economical as well as essential, lime has virtually no substitutes in most of its many, varied chemical and industrial uses. There has been some significant competition from other materials in construction and agriculture. Quicklime is also the principal raw material in calcium production.

Lime is so reactive to water and carbon dioxide that it never occurs naturally and is very perishable. Accordingly, it is manufactured as it is needed, and the supply ordinarily equals the demand. Although there are many kinds of calciners, most quicklime is manufactured in two types of kilns: Vertical kilns and rotary kilns. In the United States rotary kilns produce most of the quicklime, but abroad vertical kilns are responsible for most lime manufactured. Even in the United States, vertical kilns predominated in lime output until recent years. There are two classes of hydrators, continuous and batch hydrators; the continuous hydrator is preferred.

Many problems are encountered in quarrying, calcining, hydrating, storing, handling, and transporting. Problems at some operations include collecting and utilizing comminuted limestone waste, using byproduct carbon dioxide, and recovering or disposing of lime sludge. Particular attention is being directed continually toward the improvement of kiln design and operation, and basic research is also being conducted into the fundamental nature and properties of lime itself. So far as calcium is concerned, research deals with new methods of extraction that increase purity at lower cost; new ways of fabricating, working, and machining the unusual metal; and finding new uses for it, its alloys, and its compounds (*4*).[2]

BACKGROUND

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

In 1963, 210 lime and dead-burned dolomite plants in 38 States and Puerto Rico produced 14.5 million tons of lime valued at $199 million at the plant. Next to sulfuric acid lime is the largest tonnage chemical produced in the United States.

There has been a steady reduction in the number of lime plants in the United States for the past 60 years. In 1963 the 67 plants, or 30 percent of the total plants reporting, had an annual output of less than 10,000 tons each. The 19 plants reporting production of 200,000

[1] Commodity specialist.
[2] Italicized numbers in parentheses refer to the items in the list of references at the end of this chapter.

tons or more accounted for 49 percent of total lime. Ohio, Michigan, and Missouri, in descending order, are the principal lime producing States, while the three largest consumers of lime also in descending order are Ohio, Michigan, and Texas. Most of the lime produced in the United States is high-calcium lime derived from limestone containing over 95 percent calcium carbonate, from marble waste and from shell. Most Ohio lime is dolomitic. Dolomitic lime also comes from Massachusetts, Eastern Pennsylvania, Illinois, Wisconsin, Utah, Nevada, and California. In Texas and Louisiana much high-calcium lime is derived from shell. Less than 5 percent of the total crushed limestone or 21.5 million tons produced in 1963 was used for making lime and dead-burned dolomite.

DEFINITION OF TERMS, GRADES, TESTS, AND SPECIFICATIONS

The calcination of limestone, shells, or other calcium carbonates produces *quicklime*. *Lump lime*, in pieces 5 to 12 inches in size, is a product of stationary or shaft kilns. The calcination process does not change the shape or size of the original limestone charge, but the porosity of the lumps is considerably increased by voids left by the removal of carbon dioxide. The reaction involved in calcining is: $CaCO_3$ + heat = CaO (lime) + CO_2 (carbon dioxide). Lump lime may be crushed or ground to customers specifications. A smaller sized product, resulting from the calcination of ½ to 2½ inch size limestone, is obtained from rotary kilns and is known as *pebble lime*. *Hydrated lime* is produced from ground quicklime by the addition of carefully controlled amounts of water in intermittent or continuous mechanical hydrators. This hydration process gives a stable, finely divided dry material, 95 percent of which passes through a 200 mesh screen. For many uses hydrated lime is more satisfactory than lump lime and is easier to store and transport. A paste of slaked lime and water is termed *lime putty*, and a suspension of slaked lime in water is called *milk of lime*.

Dolomite, calcined at a high temperature, with the addition of a stabilizing agent such as iron oxide or mill scale, becomes relatively inert to the action of atmospheric moisture and carbon dioxide and is known as *dead-burned dolomite* (*5*). This refractory material is granular and can be shipped in bulk. Dead-burned dolomite statistics have been included with the lime statistics by the Federal Bureau of Mines. A semiburned dolomite produced at temperatures below 1,900° F is used for water treatment.

The general term *lime* is often misconstrued to include materials other than the oxides and hydroxides of calcium and magnesium and is applied without discrimination to limestone, marls, shell, and gypsum. "Agricultural liming material", according to the Association of Official Agricultural Chemists is "material whose calcium and magnesium content is capable of neutralizing soil acidity." In industry the term lime is used to denote calcium carbonate, calcium sucrate, and calcium acetate. *Hydraulic lime* is produced by calcination of limestone containing enough aluminous and siliceous material, such as clay minerals, to form a substance that will slake and set or harden under water. Feeble hydraulic limes contain 5 to 10 percent argilaceous material, and highly hydraulic limes contain 15 to 30 percent. The slow rate of setting and low strength of hydraulic limes make them inferior to the conventional portland cements for most construction uses. *Hydraulic limestone* contains the proper amounts of silica and alumina so that a hydraulic lime, which will slake and set or harden under water, will be produced on calcining. Specifications for different uses of lime are given in a report by the National Lime Association (*3*), and periodically in reports of the American Society for Testing and Materials (*1*).

Commercial limes include such impurities as alumina, silica, and iron oxide. Alumina and silica in lime often indicate the presence of clay and less often mica and feldspar in the original limestone. Also the presence of silica may indicate these silicates, or admixed quartz, chalcedony, or calcium and magnesium silicates. The presence of over 5 percent silica in a limestone renders it unsuitable for limemaking. To be used to manufacture chemical or metallurgical lime, the limestone should contain less than 1 percent alumina and less than 2 percent silica. Iron oxide in lime is derived from limonite, pyrite, or siderite in the limestone, and their presence may result in off color lime. Organic or carbonaceous impurities are less objectionable, because they are removed as carbon dioxide during calcination. Sulfur from pyrite and phosphorous from apatite and collophane, on the other hand, are undesirable contaminants in chemical and metallurgical lime and should not exceed 0.05 and 0.02 percent respectively. The inherent dangers to public health because of the presence of lead, zinc, and other metals or minerals in some agricultural lime is under investigation.

TECHNOLOGY

Calcium is the fifth most abundant element in the earth's crust and constitutes 3.4 percent

of it by weight. Calcium oxide is the fourth most abundant oxide in the earth's crust, amounting to 4.8 percent. Lime and calcium chloride are the principal sources of elemental calcium or calcium metal, its alloys, and its compounds used for metallurgical purposes. Calcium is a silvery-white, soft, light bivalent metal of the alkaline-earth group. It has a Rockwell B hardness of 36 to 40. On exposure to air, it tarnishes quickly, acquiring a thin bluish film. The metal oxidizes rapidly in the presence of moisture or at a temperature above 570° F. Calcium imparts a brilliant yellowish-red light to the test flame. Its atomic number is 20, atomic weight is 40.08, specific gravity at 70° F, 1.55, it melts at 1,560° F, and boils at 2,625° F. At 840° F, calcium changes from the face-centered cubic system to the body-centered cubic or hexagonal close-packed crystal system.

Although calcium is much too unstable to occur naturally, its compounds are very common in nature. It occurs as carbonates (limestone, marble, chalk, calcareous marl, shell, calcite, aragonite, dolomite, and ankerite); sulfates (gypsum and anhydrite); phosphate (apatite); fluoride (fluorspar or fluorite); and in many silicate minerals. Virtually all natural waters carry dissolved calcium compounds. Calcium is usually the most abundant nonaqueous element in fresh water. On the average it constituted 20.3 percent of the solid mineral residue of fresh water, having an average salinity of 146 parts per million, in a recent worldwide study. Compounds of calcium are essential constituents in the bodies of most animals and plants. Bones, teeth, and shells are calcium compounds, and on the average, calcium amounts to 0.5 percent of the dry weight of terrestrial plants and 20 percent of their ash.

Mining and Milling

Limestone and dolomite used in manufacturing limes are obtained from open pits and underground mines. Mining and quarrying are discussed in the "Stone" chapter. Elimination of impurities, careful sizing, and careful selection of stone are required in mining and quarrying to produce lime of uniform composition and size or of special composition. Crushers are used to break the quarried limestone and screen to size it (*14*).

Lime Processing

Crushed stone composed of calcium carbonate yields carbon dioxide gas when heated to the dissociation temperature of about 1,400° to 1,700° F, and highly basic calcium oxide, or quicklime, remains. When treated with water the quicklime slakes, giving off heat and increasing in volume to form calcium hydroxide or hydrated lime. Both quicklime and hydrated lime react slowly with water vapor and carbon dioxide in the air to return to the original, more stable, calcium carbonate.

Limestone is calcined in shaft and rotary kilns. Quicklime is the immediate product of calcination. Theoretically, 1,000 pounds of limestone will produce 560 pounds of quicklime. In many modern lime plants, a significant proportion of the quicklime output is converted to hydrated lime by processing it one step further in a batch or a continuous hydrator. The 560 pounds of quicklime require 180 pounds of water to be completely hydrated; thus 1,000 pounds of limestone will theoretically yield 740 pounds of dry hydrated lime. These theoretical yields of quicklime and hydrated lime represent the ideal maximum that is never realized, and smaller quantities are always produced under the less than ideal conditions of actual manufacturing. Over one-fifth of the lime produced in the United States is hydrated. Modern methods of lime manufacture, including quarrying or mining, preparing, calcining, and hydrating, have been published. Carefully classified, crushed limestone, ranging from ¼ inch to 2½ inches in size, is fed into the higher end of the rotary kiln and pebble quicklime is taken from the lower end. Rotary kilns vary from 6 to 11½ feet in diameter and from 60 to 400 feet in length, although 150 feet is the most common length. To reduce fuel costs, most rotary kilns have preheaters at the feed end and coolers at the discharge end. The rotary kiln is considered to have the highest capacity of all limekilns. Rotary kilns produce the greatest lime tonnage per man-hour of all limekilns, are the most completely automatic and instrumented kilns, permit the highest degree of quality control, and produce the most uniform quicklime. On the other hand, they require a larger capital investment and have higher unit fuel costs than efficient vertical kilns.

Vertical or shaft kilns, into which crushed and broken limestone (usually 4- to 8-inch size, but sometimes up to 100 pounds, or "1-man" size) is fed at the top and lump quicklime is removed from the bottom, are constructed in many forms and modifications. Many are 35- to 75-foot-high, steel-covered, refractory-lined, cylindrical structures with 10- to 24-foot cross-sectional diameters. Others have a square or rectangular cross section. The most complete vertical kiln has five sections or zones from top to bottom: Preheating, calcining, finishing, cooling, and storage. Into a mixed-feed vertical kiln, both crushed limestone and coal are fed at the top, either in alternate layers or thoroughly mixed. A mixed-feed vertical kiln has the economical advantage of more complete

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combustion of fuel, but its quicklime is contaminated with ash. Captive-lime plants in the alkali and sugar industries, where ash contamination of quicklime is unobjectionable, have mixed-feed vertical kiln. Modern, large-capacity vertical kilns produce 80 to 160 tons of quicklime a day. Vertical kilns have a lower fuel cost, smaller capital investment and greater flexibility in operation than rotary kilns (*2*).

Two new types of kilns have come into use since World War II: The FluoSolids kiln and the Ellernan kiln. The FluoSolids kiln is a vertical kiln that uses limestone reduced to 10-mesh or smaller, which is preheated in stages. This kiln has three compartments from top to bottom—preheating, calcining, and cooling. It is advantageous to use wherever limestone and lime granulate or crumble, and it combines a high capacity with economical fuel requirements. The calcining chamber of the Ellernan kiln has horizontal tunnel beams that stir the downward-moving limestone feed to insure uniform calcination. It is a continuous kiln and produces a pebble lime ¼ inch to 1½ inches in size.

At first limekilns were fired with wood; then coal supplanted wood; and now natural gas and fuel oil are displacing coal. Limestone does not freely release carbon dioxide until the kiln temperature is 1,800° F, which is well above the dissociation temperature. Actual temperature in lime-burning is usually at least 2,000° F, and may reach 2,500° F, to reduce the time required for complete calcination.

Refractory lime or dead-burned dolomite is usually calcined in rotary kilns, but the calcining temperature is higher (over 2,800° F) and the burning time is longer. Only true dolomite is used because more calcic stone, even when dead-burned, is still too reactive to moisture.

Hydrated lime is manufactured by slowly adding water to ground quicklime in a hydrator or slaker. Both batch and continuous hydrators are used. The quicklime-water mixture is mechanically agitated to insure thorough mixing. To produce a dry hydrated lime, the theoretical water to quicklime ratio of 18 : 56, or about 1 : 3, is closely followed, although some excess water is needed to offset water lost as steam formed by the heat of hydration. An air separator eliminates the uncalcined material and most of the silica after hydration.

Normally hydrated dolomitic lime consists of calcium hydroxide and magnesium oxide with little, if any, magnesium hydroxide. About 1940, actually hydrated dolomitic lime was introduced and called highly hydrated dolomitic lime. It is produced by hydrating dolomitic quicklime in an autoclave at the necessary pressure. Some soft dolomitic limes have been completely hydrated by adding water to quicklime in silos or retention bins. Highly hydrated dolomitic lime is usually milled and bagged.

Calcium Extraction

The metal calcium was first isolated by Sir Humphry Davy in 1808 by the electrolysis of a mercury-lime mixture followed by distillation of the mercury from the resulting amalgam (*7*). At a later date H. Moissan prepared the metal by reducing calcium iodide with sodium.

Metallic calcium is prepared industrially by the electrolysis of fused calcium choride, although the earlier Pidgeon process, in which lime (CaO) is reduced by aluminum under vacuum by the application of heat, is still used as a standby method.

The calcium initially recovered by these methods may be of only 85 percent purity. It is brought up to 95 to 97 percent purity by repeated melting, skimming, and casting in an inert atmosphere, usually argon. Calcium is distilled in an argon atmosphere when extra high purity above 99 percent is required.

The major impurities in calcium metal are calcium oxide, sodium chloride, and magnesium. Calcium is separated from sodium, when they are mixed together in an electrolytic sludge, by treating the mixture with an excess of a lower aliphatic alcohol, which reacts preferentially with sodium, dissolves the reaction product, and releases hydrogen. After the sodium has been dissolved, the calcium settles and is removed before any appreciable amount of calcium has reacted with the alcohol solution to release more hydrogen. A crystalline calcium of 94 to 97 percent purity and in 50 to 400 mesh sizes is produced which is much more reactive than ordinary grades (*10*).

To produce calcium hydride, on an industrial scale, lumps of calcium metal are heated to 750° F in a hydrogen atmosphere until all the calcium is transformed to the hydride.

USES

Although for centuries lime was used primarily for mortar, plaster, and as a disinfectant, these uses have been relegated to minor importance. Lime is now regarded as a basic industrial chemical and the starting material for a wide variety of chemicals, as well as for use in the neutralization of industrial and agricultural wastes, in high-temperature and dehydration processes, as a causticizing agent in the sulfate process of papermaking, in water softening and purification, and in the manufacture of petrochemicals and insecticides. In the iron and steel industry it is used in increasing quantities in the production of self-fluxing ores, in basic oxygen converters, and in electric furnaces. Lime

is also used for the removal of silica from bauxite ores, for the production of alumina, and in processes for the reduction of magnesium. Smaller quantities are used in the manufacture of sugar, soaps and greases, glue and gelatines, and in the leather industry for removing hair and plumping skins. In construction it is used in masonry mortars, plasters, sand-lime brick, stuccos, cement, and in solid stabilization of roads, runways, and similar projects. Table 3 indicates the tonnages produced for a variety of uses.

Calcium is a lightweight silvery-white metal. It is harder than sodium but softer than aluminum. It may be cast, extruded, machined, rolled into sheets, and drawn into wires. Its principal use is as a reductant for the refractory metals such as chromium, titanium, zirconium, hafnium and uranium (*8*). It is also alloyed with other light metals and is used to remove bismuth from lead and as a nodulizer for cast iron. It is also used as a deoxidizer during the pouring of steel ingots and as a gas absorber in the manufacture of vacuum tubes. It is used to separate argon from nitrogen by the liquid gas industry and to remove sulfur from crude oil. Calcium silicide, an electric furnace product from the reaction between lime, silica, and carbon is used as a steel deoxidizer, and calcium carbide, which upon hydrolysis yields acetylene, the basic material for a wide variety of industrial chemicals. The hydride of calcium (CaH_2), stable in oxygen to 400–500° C, is an excellent reducing agent for the conversion of acetone to mesitylene and is also used as a source of hydrogen for meteorological balloons.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Carbon dioxide, produced during calcination of limestone, is of basic importance in the carbonation of beet sugar syrup, and other lime plants recover it for sale or use in processing sodium chemicals (*9*). Excess limestone production is sold by some lime producers for use in concrete construction and for road building.

ALTERNATE MATERIALS

In its use as an alkaline reagent in the manufacture of chemicals and for many industrial uses there are no alternate materials to replace lime within a comparable price range. Finely ground limestone has largely replaced lime in agricultural uses because it lasts longer in the soil and requires less frequent application. In 1911 the use of lime for masonry mortars began declining, and utilization of cement for mortar increased. Furthermore, in building construction, gypsum plaster and gypsum wallboard and lath have largely replaced the older type of lime-sand plastered walls because of lower costs of installation. In the Southern States gypsum and anhydrite compete with lime for use in soil conditioning. Sodium, magnesium, potassium, and aluminum metals can be substituted for calcium in some uses.

SECONDARY SOURCES AND RECOVERY

Reuse of lime is customary in the paper pulp, calcium carbide, and beet sugar industries. Reclamation plants recarbonate the used lime sludge, dewater it, and recalcine (*12*). This regenerated lime accounts for approximately 26 percent of the total lime used, but including regenerated lime produced at water treatment plants, the amount entering the open market is less than 1 percent.

RESERVES

The sedimentary calcareous rocks, used in the manufacture of lime, are widespread in the United States, but occur in many degrees of purity. The high-grade limestones desired by manufacturers of pharmaceuticals, and the various chemical industries which are fundamentally based upon lime, are not as plentiful as the lower grades which may contain a wide variety of undesirable impurities. The high-grade beds, to which access is easy, are being depleted and lime-burners must go further afield for raw materials, or treat the lower grade more plentiful limestones by methods which are costly to remove these impurities (*11*). Because of the abundance of limestone deposits, no official estimates of reserves suitable for the manufacture of lime have been made. At the present time the question of reserves is not a limiting factor to the growth of the lime industry in the United States.

SOURCES OF STATISTICAL INFORMATION

Comprehensive statistics of the open-market and captive-lime industry are compiled annually by the Bureau of Mines. A less detailed, but indicative, monthly canvass is conducted of all domestic plants that produce over 10,000 tons of lime a year. This monthly survey permits observing and following national trends in lime during the interval between the annual statistics that embrace the entire industry. Lime import and export figures are published annually by the Bureau of Mines from data collected by the U.S. Department of Commerce.

PRODUCTION, CONSUMPTION, AND TRADE

In the lime industry stocks are kept low and fairly constant. Production can be increased quickly with existing facilities, and established plants are competent to supply anticipated needs.

Table 1 shows the annual lime tonnage sold or used in the United States, and table 2 shows breakdown by use and value. Ohio, Michigan, Texas, Pennsylvania, and Louisiana in descending order were the leading lime consuming States in 1963.

Because of the relatively low price of lime, foreign trade is of minor importance. In 1963, 87 percent of exported lime went to Western Hemisphere countries, which in order of decreasing quantities were, Canada, Mexico and Bahamas, and Nicaragua.

Duties on lime were unchanged from 1959; 3 cents per hundred pounds for hydrated lime, including the weight of the container, and 2½ cents per hundred pounds, including the weight of the container, on other types of lime.

STRATEGIC CONSIDERATIONS

The United States has ample supplies of limestone, shell, calcareous marl, marble, dolomite, and fuel for manufacturing whatever lime tonnage is needed. It is entirely self-sufficient in this commodity.

Lime is the lowest priced alkali obtainable and is therefore of fundamental importance in the manufacture of thousands of industrial chemicals as well as in many metallurgical processes and the more common uses for various types of construction. Metallic calcium is important as a deoxidizer and dehydrator and for its ability to form alloys with a number of other metals. However, it may be replaced, for most of these uses, by alternate alkali metals. The United States is independent of foreign lime and stockpiling for unanticipated needs is not required. Furthermore, stockpiling is impractical because of perishability, danger of fire, and expense of storage. Only by expansion of production facilities can unexpected demands be met.

TABLE 1.—*Salient lime statistics in the United States*

[Thousand short tons and thousand dollars]

	1954–58 (average)	1959	1960	1961	1962	1963
Active plants	150	154	157	220	215	208
Sold or used by producers:						
Quicklime	5,738	7,746	8,271	8,998	9,509	10,128
Hydrated lime	2,100	2,766	2,715	2,269	2,386	2,444
Refractory lime	1,997	1,988	1,949	1,982	1,858	1,949
Total	9,835	12,500	12,935	13,249	13,753	14,521
Value [1]	$124,222	$163,909	$172,733	$177,463	$186,754	$199,389
Average value, per ton	$12.63	$13.11	$13.35	$13.39	$13.58	$13.73
Open market	8,204	8,396	8,189	8,072	8,145	8,889
Captive [2]	1,631	4,103	4,746	5,177	5,608	5,632
Imports for consumption	39	35	32	37	78	101
Exports	70	53	61	30	20	17

[1] Selling value, f.o.b. plant, excluding cost of containers.
[2] Incomplete figures; before 1961 the coverage of captive plants was only partial.

TABLE 2.—*Lime sold or used by producers in the United States, by major uses*

Use	1962			1963		
	Short tons	Value [1]		Short tons	Value [1]	
		Total	Average per ton		Total	Average per ton
Agricultural	191,637	$2,636,844	$13.76	176,559	$2,582,169	$14.30
Construction	1,290,229	21,980,560	17.04	1,435,169	23,519,221	16.39
Chemical and industrial uses	10,410,501	131,074,683	12.59	10,961,576	140,229,607	12.79
Refractory lime	1,857,438	31,059,293	16.72	1,948,953	33,057,530	16,96
Total [2]	13,753,000	186,754,000	13,58	14,521,000	199,389,000	13,73

[1] Selling value, f.o.b. plant, excluding cost of container.
[2] Data may not add to totals shown because of rounding.

TABLE 3.—*Lime sold or used by producers in the United States, by uses*

[Short tons]

Use	1962			1963		
	Open-market	Captive	Total	Open-market	Captive	Total
Agriculture	192,000	----	192,000	176,000	(1)	176,000
Construction:						
Finishing lime	446,204	----	446,204	463,838	----	463,838
Mason's lime	469,746	74,165	543,911	457,376	----	457,376
Soil stabilization	275,914	73	275,987	395,577	83	395,660
Other	24,127	----	24,127	39,392	78,903	118,295
Total [2]	1,216,000	74,000	1,290,000	1,356,000	79,000	1,435,000
Chemical and other industrial:						
Alkalies (ammonium, potassium, and sodium compounds)	26,693	3,068,236	3,094,929	11,064	3,129,125	3,140,189
Brick, sand-lime, slag and silica	25,457	----	25,457	32,267	----	32,267
Calcium carbide	565,375	361,339	926,714	583,869	368,147	952,016
Glass	255,861	----	255,861	243,717	----	243,717
Other chemical uses [3]	728,756	530,165	1,258,921	632,131	838,327	1,470,458
Metallurgical uses:						
Aluminum	50,164	280,253	330,417	91,559	90,284	181,843
Copper smelting	106,503	199,689	306,192	107,574	178,457	286,031
Magnesium	26,802	336,770	363,572	17,814	93,539	111,353
Other nonferrous	3,814	35,957	39,771	4,720	----	4,720
Ore concentration [4]	52,856	2,427	55,283	62,226	2,840	65,066
Steel flux	1,574,867	74,536	1,649,403	1,842,789	71,643	1,914,432
Miscellaneous steel processing (wiredrawing etc.) [5]	32,283	35	32,318	19,190	41,664	60,854
Paper and pulp	610,429	33,944	644,373	747,896	40,212	788,108
Sewage and trade-wastes treatment	117,709	15,698	133,407	202,478	43,798	246,276
Sugar	30,152	515,008	545,160	25,497	585,735	611,232
Water softening and treatment	741,593	7,130	748,723	852,672	342	853,014
Total [2]	4,949,000	5,461,000	10,411,000	5,477,000	5,484,000	10,961,000
Refractory lime	1,787,000	71,000	1,858,000	1,880,000	69,000	1,949,000
Grand total [2]	8,145,000	5,608,000	13,753,000	8,889,000	5,632,000	14,521,000

[1] Included with open-market agriculture lime to avoid disclosing confidential data.
[2] Data may not add to totals shown because of rounding.
[3] Includes alcohol, calcium carbonate (precipitated), coke and gas, food and food byproducts, insecticides, medicine and drugs, explosives, oil-well drilling, paint, petrochemicals, petroleum refining, rubber, tanning, salt, miscellaneous and unspecified uses.
[4] Includes flotation, cyanidation, bauxite purification, and magnesia manufacture.
[5] Includes wiredrawing, and various metallurgical uses.

PRICES

Prices for lime fluctuate according to demand, type, and source of supply. The average price of $13.73 per ton reported in 1963 represents an increase of only 18 percent over 1953. Prices of many other commodities rose much more in this period; however, the relatively stable price of lime does not reflect a lessening of demand but rather increased efficiencies in production and distribution. Output of open-market lime, exclusive of refractory lime, during the period 1953–63 increased 22 percent, although production of lime for agricultural uses declined considerably. Comparative figures for the production of captive and regenerated lime are not available. Prices are quoted for lime with or without containers, both at the plants and when delivered at metropolitan centers. In 1964 prices for common hydrated lime varied from a high of $44.00 per ton in Denver to a low of $2.70 per ton in Birmingham.

The price for calcium metal, of 98 percent purity, was quoted in 1964 at $0.95 per pound in lots of over 1 ton. For calcium of 99.9 percent purity it was available in small lots for $2.60 per pound f.o.b. plant. Imports of calcium in 1963 were 43 percent lower than in 1962.

TAXES

The depletion allowance on limestone and dolomite used in manufacturing lime is 15 percent. There has been no depletion allowance on lime, but recent court cases have, in some instances, upheld depletion allowances based on the selling price of finished product.

TRANSPORTATION AND STORAGE

Risk of fire, perishability, and storage expense are foremost objections to maintaining large stocks. Quicklime must be stored in multiwalled, water-proofed bags, or in watertight tanks to prevent the dangerous consequences of uncontrolled hydration, and even hydrated lime should be stored in airtight containers if gradual deterioration by air-slaking is to be prevented. Accidental contact of stored quicklime with water must be avoided. Even exposure to dampness results in slaking, and enough heat may be generated to start a fire if quicklime is stored in contact with combustible materials.

Quicklime must be kept away from open doors and all flammable materials, and its dust can cause severe burns (*6*). In general, quicklime should not be stored longer than 3 months and hydrated lime not more than 1 year (*18*).

Since quick and hydrated lime are relatively inexpensive, perishable, bulk commodities, proper transportation is costly and discourages foreign and long-distance domestic movement. Quicklime is shipped in sizes ranging from pulverized to 8 inches in diameter. Some lump and pebble quicklime is pulverized and bagged for shipment, but most lump and pebble lime is sorted as it is taken from the kiln and shipped in bulk in covered hopper cars, box cars, and container cars. Hydrated lime is always pulverized and is usually shipped in bags. The shipping of lime in self-unloading bulk trailers is becoming increasingly important, and in some localities lime slurries are conveyed by pipeline to the point of use. Forty- to 50-pound natural kraft paper is used by manufacturers and distributors for lining freight cars and trucks. This paper reduces chaffing of bags and assures delivery of a clean product. More expensive flame-resistant paper is used where a fire is a danger (*18*). To retard slaking dead-burned dolomite is frequently sprayed with oil before shipment (*4*). The principal hazard in handling and shipping calcium metal is the risk of fire from hydrogen formed by the reaction of the metal with moisture. To counteract this, metallic calcium is shipped in lump form under an argon atmosphere within special containers (*13*), and when finely divided, in a nitrogen atmosphere within special containers. For long storage calcium lumps of 1 to 130 pounds may be carefully freed from fines and packed in iron drums with seams and lids soldered.

RESEARCH

Three types of research that benefit the lime industry are conducted by private industry and universities: (1) finding new uses for lime (*17*); (2) improving methods of manufacturing lime (*16*); (3) basic lime research. Every year brings forth new patented processes for burning lime and for methods by which lime may be used in making new basic chemical products. These advances do not ordinarily come from within the lime industry itself but they are extremely important because they augment the national demand for lime. Although most new lime uses are chemical and industrial, some research is related to construction (*3*).

The lime industry is most directly involved in research on methods of production and improvements in quality. Producers of captive lime conduct research, within their own laboratories, to develop more efficient methods of lime burning and to promote efficiencies in the use of lime for their particular products. Continuing efforts are made to lower fuel ratios, extend refractory life, and to extend automation to many branches of the lime-burning process. Dust control, cleaning of kiln-exhaust gases, recovery of byproduct carbon dioxide, and improving efficiency of hydration processes are all subjects for research by the lime industry and by manufacturers of equipment. Basic lime research is conducted by the National Lime Association, the lime industry's central organization. The Association has no research laboratory of its own but supports research at some university laboratories, reports results of research accomplished by other organizations, and conducts training classes for certain users of lime.

OUTLOOK

No drastic increases are anticipated in the quantity of lime produced for its multitude of uses, and although prices may continue their upward trend, competition should act to stabilize them. Present capacity of plants to produce lime is ample, both for the present and for some few years to come. Based upon general national trends, production of primary open-market lime should amount to 11 million tons by 1980. The estimated production of lime for all uses in 1980 is 30 million tons.

Improved methods for autoclaving sand-lime brick have resulted in production of bricks greatly superior to those produced 40 years ago and should increase sales of lime for this purpose. Growing insistence on control of stream pollution should increase the market for lime used to reduce acidity of mine water and as a coagulant for precipitating industrial wastes. The use of hydrated lime to stabilize subgrades of roads and in preparing footings for buildings may be expected to increase in areas in which the soil consists largely of plastic clays. Demand for lime in production of steel, by the various basic-oxygen processes, should grow as the older open hearths are replaced by converters.

Technological changes in industrial and chemical processes, which use lime, may drastically affect some producers. The once firmly established use of calcium carbide for production of acetylene, on which many chemical processes was based, may decline because of substitution of propylene and ethylene for acetylene.

Substitution of gypsum wallboard and gypsum plasters for construction in place of lime mortars, plasters, and stuccos, appears likely to continue.

Demand for calcium metal for use in purification of gases, as a getter in high-vacuum technology, and as a reductant in metallurgy of rare metals is not expected to increase greatly.

PROBLEMS

The search for new markets for lime with the accompanying need for research to satisfy the type and grade requirements of the new lime consumers is an ever-present problem. The rapidly changing technology, in many consumer industries, may eliminate some well established uses for lime. New developments in kilns, giving lower fuel consumption, reduced maintenance costs, better products, or which are more easily adapted to automation, may cause some older plants to be less competitive. The continuing problems of rate of kiln feed, heat control removal of dust, storage, hydration, and transportation, are all matters for intensive and continuing research. Increased use of alternate materials such as gypsum and other substitutes for plastering and wallboard reduces demand for certain types of lime. The regeneration and sale of lime from miscellaneous chemical processes offers competition to some producers of open-market lime. The storage and disposal of regenerated lime is a problem to the paper pulp, sugar, and chemical industries. With the exception of a few producers of exceptionally high-purity lime, sales are limited to areas in which transportation costs are moderate.

The demand for calcium metal, used in pyrometallurgy, and for many other purposes, is accompanied by problems in production, use, and storage (*5*, *19*). Costs are high because of the discontinuous nature of production and the need for high-purity salts used in electrolytic processes. In addition, electrolytic processes for producing calcium are critically affected by contamination from refractories and the alloys used to make the cells. The cells used in the electrolytic reduction of calcium fail because of burnthroughs, cracking, and corrosion. Metallothermic methods for the production of calcium are complicated by the necessity of using both high temperatures (to 1,700° C) and extremely high vacuum.

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LITHIUM

By Donald E. Eilertsen [1]

LITHIUM is the lightest of all metals, but is used mainly in compounds for varied applications such as multipurpose greases, batteries, welding, ceramics, air conditioning, bleaching, and generation of hydrogen for buoyancy purposes. Nevertheless, extremely lightweight lithium-magnesium alloys are promising aerospace and industrial structural materials.

Spodumene from pegmatites and dilithium-sodium-phosphate from brines are the current raw materials used to make lithium and its compounds.

Foreign lithium minerals are recovered by hand-sorting methods while domestic spodumene is obtained by mechanized mining and milling methods. Spodumene is converted to lithium compounds by either an acid or an alkali method. The processors of lithium mineral source materials to lithium primary products in the United States are Foote Mineral Co., at Sunbright, Va., and Exton, Pa.; Lithium Corp. of America, Inc., at Bessemer City, N.C.; and American Potash & Chemical Corp., at Trona, Calif.

Lithium compounds are used in multipurpose greases, nuclear energy, air conditioning, storage and dry cell batteries, welding and brazing, ceramics, glass, bleaches, catalysis, and preparing hydrogen.

Lithium metal's principal uses are in alloying, preparation of compounds, purification of steels, copper, and copper alloys, and production of synthetic rubber. Various lithium minerals also have ceramic applications.

Moderate growth of the lithium industry is anticipated. Problems of the industry include development of new uses and markets and further development of the technology.

BACKGROUND

Germany was the first producer of lithium minerals and remained the largest producer until 1886. The leadership was then held by France until the early 1900's. The United States led from 1900 until 1953, and since then Southern Rhodesia has been the leader.

The first commercial production of lithium minerals in the United States took place in 1898 when 30 tons of spodumene was shipped from the Etta Mine in the Black Hills, S. Dak. Other mines began to produce lithium minerals, and by 1910 the U.S. output, all from South Dakota, reached 238 tons.

Dilithium-sodium-phosphate, from Searles Lake, Calif. brines in 1938, and spodumene flotation concentrate from Kings Mountain, N.C. pegmatites in 1953 became important commercial sources of lithium.

European production of lithium compounds dates back before 1900 whereas U.S. production was started in 1901 by two firms in New Jersey. Three firms in the United States process lithium minerals to lithium compounds at the present time.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Foote Mineral Co. mines spodumene ore from pegmatite and produces spodumene flotation concentrate at Kings Mountain, N.C.; and American Potash & Chemical Corp. recovers crude dilithium-sodium phosphate from Searles Lake brines at Trona, Calif. In addition to this some amblygonite has been produced in South Dakota.

Currently, three firms in the United States process lithium minerals to lithium compounds. They are Foote Mineral Co. at Sunbright, Va.

[1] Commodity specialist.

and Exton, Pa.; Lithium Corp. of America, Inc., at Bessemer City, N.C.; and American Potash & Chemical Corp. at Trona, Calif.

Elsewhere in the free world in recent years, lithium compounds have been produced in the United Kingdom, France, West Germany, Southern Rhodesia, Brazil (*8*),[1] Italy, and Quebec.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Lithium is soft, silver-white, and the lightest of all metals 0.534 g./cm.^{3} at 20° C. Some of its other properties as follows (*6*) :

Atomic number	3
Atomic weight	6.94
Melting point, °C	179
Boiling point, °C	1,317
Heat of fusion, calorie per gram, (179° C)	103.2
Heat of vaporization, calorie per gram (1,317° C)	4,680
Heat capacity, calories per gram per degree C. (0° C)	0.784
Coefficient of linear thermal expansion per degree C, (20° C)	56×10^{-6}

Lithium metal reacts violently with water to form hydrogen and lithium hydroxide, but the heat involved is not sufficient to ignite the hydrogen.

The chemical composition and lithia (Li_2O) contents of five sources of lithium are shown in table 1.

TABLE 1.—*Lithium source materials*

Mineral	Chemical composition	Theoretical Li_2O content (percent)	Approximate range of Li_2O in commercial mineral (percent)
Spodumene	$LiAlSi_2O_6$	8.0	4–7
Lepidolite	$(OH, F)_2KLiAl_2Si_3O_{10}$	3.9	3–3.5
Amblygonite	$LiAl(F,OH)PO_4$	10.1	8–9
Petalite	$LiAl(Si_2O_5)_2$	4.8	3.5–4.5
Dilithium-sodium-phosphate.	Li_2NaPO_4	22.6	19–21

TECHNOLOGY

Mineralogy and Geology

The lithium content of the earth's crust has been estimated to be 65 parts per million while in sea water the lithium content is 0.1 part per million. Approximately 145 minerals in the earth's crust contain lithium but only spodumene, lepidolite, amblygonite, petalite and eucryptite from pegmatites are commercial sources of lithium. In addition to these minerals, dilithium-sodium-phosphate, from California brines, is an important commercial lithium source.

Lithium minerals have been found in heterogeneous pegmatites where the minerals occur in enriched zones, filled fractures, and replacement bodies such as in the Black Hills, S. Dak. and elsewhere, and also unzoned or homogeneous pegmatites where the mineral constituents are somewhat evenly distributed as in the extensive spodumene deposits in the area of Kings Mountain, N.C., which are now being worked for spodumene.

Lithium is also known to occur in sedimentary deposits such as clays and shales.

Mining

Spodumene and other lithium minerals have been mined from pegmatites by open pit and underground methods of mining, sometimes while mining for these minerals alone but more often while also mining for coproducts such as feldspar, mica, quartz, and sometimes beryl, columbite, and tantalite.

Spodumene ore (pegmatite) is mined in North Carolina by Foote Mineral Co. from 20-foot benches in a large open pit employing large-scale mechanized equipment such as wagon drills for primary drilling, 5-ton drop ball for secondary breaking, large mechanical shovels to load, and huge trucks for haulage (*4*). Diamond drill exploration of the deposit is kept well ahead of mining (*5*).

Milling

Lithium minerals are recovered by hand-sorting methods in many parts of the world, but in North Carolina spodumene is currently being recovered from pegmatite type ore by crushing, screening, milling, and flotation (*3*).

In California, dilithium-sodium-phosphate is recovered by treating burkeite salt, the concentrate obtained after evaporation and subsequent separation of the brine, with a fatty acid derivative to which is added a light mineral oil. The dilithium-sodium-phosphate is floated by aeration, and the resulting froth is filtered and dried (*2, 8*).

Extraction

Lithium compounds are processed from spodumene by one of two methods—one is an acid treatment, the other is an alkali treatment (*8*). In the first method alpha spodumene is converted to beta spodumene by calcining at critical temperatures. Sulfuric acid is added, and the mixture is heated to form lithium sulfate. The lithium sulfate is leached from the mass, neu-

[1] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

tralized with limestone, and filtered. Soda ash is added to the aqueous solution of lithium sulfate to precipitate lithium carbonate. This is the basic material from which other compounds are derived. Calcium hydroxide is added to the lithium carbonate to form lithium hydroxide monohydrate. Lithium chloride is produced by reacting lithium carbonate with hydrochloric acid.

The second method involves stage-calcination of the spodumene with powdered limestone and hydrolyzing with steam to produce a soluble lithium hydroxide.

Lithium metal is produced by electrolysis of a fused mixture of lithium chloride and another alkali salt, such as potassium chloride. Lithium hydride is produced by reacting hydrogen and lithium metal. The addition of ammonia to lithium hydride produces lithium amide.

USES

A large variety of applications have been developed for lithium-bearing materials, especially for lithium compounds (*1*).

Five lithium minerals have industrial uses: Spodumene as a source of lithia in chemical and certain ceramic processes; amblygonite as a source of lithia, alumina, and phosphate in glaze and enamel frits and low-temperature glass bond; lepidolite and petalite as material for glass and porcelain enamel ground coats, ceramic body glazes, and fluxes; and eucryptite for various applications. Petalite is also used as a constituent of low-expansion heat-resistant bodies.

Lithium compounds have numerous uses and are shown in table 2.

Lithium metal is used metallurgically as an alloying element, scavenger, and degassifier for stainless and mild steels, and deoxidizer in melting copper and copper alloys. Lithium is also used as a raw material for preparing lithium alkyls and other organo compounds, catalyst in the production of synthetic rubber, selective reducing agent in organic synthesis, and intermediate in vitamin A production. The element also can be used for reactor cooling, heat transfer fluid for high temperature applications, and rocket fuel.

Lightweight lithium-magnesium alloys are attracting attention for structural applications in aerospace vehicles and in industrial uses.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Lithium-bearing pegmatite deposits usually contain other potentially marketable mineral materials, such as feldspar, quartz, mica, columbite, tantalite, beryl, and monazite. In some lithium operations one or more of these are recovered as coproducts, but usually it has not been economically feasible to recover these materials.

Coproducts such as bromine, potash, borax, sodium sulfate, and sodium carbonate are recovered with dilithium-sodium-phosphate from Searles Lake, Calif., brine.

TABLE 2.—*Uses of some lithium compounds*

Use	Lithium compound								
	Bromide	n'Butyllithium	Carbonate	Chloride	Citrate	Fluoride	Hydride	Hydroxide	Stearate
Absorb carbon dioxide							X		
Air conditioning	X			X					
Alkaline batteries							X		
Bath salts for heat treating				X					
Catalyst		X	X				X		
Ceramic raw material			X						
Chemical reducing agent							X		
Clay conditioning agent					X				
Cosmetics									X
Dehumidifier	X			X					
De-icing				X					
Dispersion stabilizer					X				
Dystuffs			X						
Glaze frits, lithia source						X			
Greases								X	X
Heat transfer medium				X					
Lithium-6 isotope								X	
Lubricant in powder metallurgy									X
Nuclear shielding							X		
Organic synthesis							X		
Pharmaceuticals		X							
Porcelain enamel, lithia source						X			
Raw material for various lithium compounds							X		
Raw material for lithium metal				X					
Refrigeration				X					
Source of hydrogen							X		
Waxes									X
Welding and brazing fluxes			X	X		X			

ALTERNATE MATERIALS

Lithium is so desirable in most of its uses that few materials are substituted for it.

In ceramics, lead can be substituted for lithium in many instances, but it is less efficient in many ways and may be toxic.

In greases lithium compounds impart water resistance and lubricating properties over extremes of temperatures. These properties apparently cannot be gained if other compounds, such as calcium, barium, or strontium compounds were used as the base component. Certain military grease performance specifications have been met only by lithium base greases.

Although lithium hydride is one of the most efficient hydrogen carriers known, for economic reasons it has been substituted by other efficient but less expensive hydrogen carriers such as calcium hydride.

RESERVES

The indicated and inferred resources of lithia in domestic pegmatites containing at least 1 percent lithia and in brines containing 0.015 percent lithia were estimated in 1955 (*7*). The indicated resources of lithia, totaling 144,000 tons Li_2O content, are located as follows: Tinspodumene belt of pegmatites in North Carolina, containing spodumene mostly but some amblygonite—40,000 tons; Black Hills pegmatites in South Dakota, containing spodumene mostly but some amblygonite and lepidolite—12,000 tons; pegmatite districts in New England, Colorado, Arizona, New Mexico, California, and Wyoming, containing spodumene mostly but some amblygonite and lepidolite—2,000 tons; and Searles Lake, Calif., brine—90,000 tons. The inferred resources of lithia, totaling 1,244,000 tons of Li_2O content, are in the spodumene belt of pegmatites in North Carolina (1,240,000 tons) and in Black Hills pegmatites (4,000 tons).

Significant resources of lithium minerals have been established in several foreign countries. Canadian deposits north of Val d'Or, Quebec, containing 20 million tons of spodumene ore averaging 1.15 percent lithia, have 230,000 tons of Li_2O. Deposits on the north shore of Bernic Lake, Manitoba, contain 9 million tons of spodumene-lepidolite-amblygonite ore averaging more than 2 percent lithia, have more than 180,000 tons of Li_2O. Five deposits in the Bougouni region, Republic of Mali, Africa, are reported to contain 1.3 million tons of spodumene ore averaging 1.3 percent lithia or 17,000 tons of Li_2O. Bakita deposits in Southern Rhodesia contain 6 million tons lepidolite-spodumene-petalite-eucryptite ore averaging 2.9 percent lithia or 174,000 tons of Li_2O. Pegmatite deposits southwest of Kalgoorlie, Western Australia, were reported to be promising for lithium—one deposit alone contains about 428,000 tons of ore averaging 1.9 percent lithia or 8,100 tons of Li_2O.

The Atomic Energy Commission has a stock of lithium hydroxide devoid of lithium-6 isotope.

SOURCES OF STATISTICAL INFORMATION

The Bureau of Mines canvasses annually for domestic lithium mineral production and recently for consumption, but not for lithium products derived from utilizing lithium minerals. The Department of Commerce canvasses the domestic lithium-producing industry for production data on primary lithium products. Statistical data on imports of lithium minerals and certain lithium compounds are compiled by the Bureau of Census, but no data are available on exports.

Data on world production of lithium minerals are compiled by the Bureau of Mines from information supplied by Foreign Service dispatches, official publications of the mining departments of the respective countries, and from other sources.

PRODUCTION, CONSUMPTION, AND TRADE

Data on lithium mineral and compound output from mines in the United States are shown in table 3.

TABLE 3.—*Shipments of lithium mineral concentrate and compounds from mines in the United States*

Year	Short tons	Value (thousands)	State (listed in order of magnitude)
1950	9,306	$580	S. Dak., Calif., N. Mex., and Maine.
1951	12,897	896	S. Dak., N.C., Calif., and Ariz.
1952	15,611	1,052	S. Dak., N.C., and Calif.
1953	27,240	2,134	N.C., S. Dak., Calif., and Colo.
1954	37,830	3,126	N.C., S. Dak., Calif., and Colo.
1955–57	(1)	(1)	(1).
1958–63	(2)	(2)	N.C., Calif., and S. Dak.

[1] Data not available.
[2] Data withheld to avoid disclosing individual company confidential data.

Record production of these materials occurred in 1959 and was followed by a very sharp decline in production. The trend in recent years is again upward.

Starting in 1964 a canvass is being made on the consumption of lithium source materials in the United States. Quantitative data on annual outputs of lithium metal, alloys, and compounds are not available for publication.

Imports of lithium minerals into the United States for the period 1951–58, not necessarily complete, were reported as follows: 1951–55 (annual average)—19,978 short tons, 1956—114,772 tons, 1957—79,617, and 1958—192,803 tons (*8*). Import figures on lithium minerals, reported by the Bureau of the Census since 1960, are shown in table 4.

As of August 31, 1963, lithium minerals are imported duty free. Lithium metal and lithium compounds are dutiable at 25 percent and 10.5 percent ad valorem, respectively.

TABLE 4.—*U.S. imports of lithium minerals by countries*

[Short tons]

Year	Argentina	Brazil	Canada	British East Africa	Rhodesia and Nyasaland	Mozambique	Republic of South Africa	Total	
								Quantity	Value [1]
1960	110	33	1,409	----------	49,547	----------	----------	51,099	$1,358,573
1961	----------	----------	2,115	----------	22,462	----------	2,252	26,829	776,578
1962	----------	----------	330	----------	23,603	[2] 5,661	1,115	30,709	1,006,037
1963	----------	----------	----------	1,127	19,088	[2] 2,248	----------	22,463	663,891

[1] Value at port of exportation.
[2] Reported as Mozambique but believed by the Bureau of Mines to be from Southern Rhodesia via Mozambique.

STRATEGIC CONSIDERATIONS AND GOVERNMENT PROGRAMS

The domestic reserves of spodumene and lithium-bearing brines are adequate to sustain the lithium producing industry indefinitely. Domestic sources of lepidolite, amblygonite, and petalite are not available. Consequently, the ceramic industry and any lithium production that may develop from the use of these special materials will probably have to come from imports.

No special considerations are given to lithium minerals for Government assistance in exploration and stockpiling.

PRICES

Prices for lithium minerals are on a buyer and seller basis, and they are seldom published. The average price of imported lithium mineral concentrate at the port of exportation in 1963 was $29.55 per short ton. The principal lithium compounds, lithium carbonate and lithium hydroxide, sell for about 60 and 55 cents per pound respectively. Prices on these and other compounds can be found in the issues of Oil, Paint, and Drug Reporter. Lithium metal, 99.5-percent pure, was quoted at $9 to $11 per pound throughout 1963 in the issues of the E&MJ Metal and Mineral Markets.

TAXES

The domestic depletion allowance is 23 percent whereas the foreign depletion allowance is 15 percent.

RESEARCH

Industry-sponsored research under way on lithium includes studies on improving processes and qualities of products, developing new uses and new products, and recovering various minerals including lithium from brines.

Some research on lithium is Government sponsored. Studies are mostly on the properties of various lithium materials and on the occurrence and recovery of various metals including lithium from saline waters.

OUTLOOK

The outlook for the lithium industry is one of optimism—moderate and steady growth in demand is predicted thus narrowing the gap between production capacity and industrial consumption. Market expansion and development will be emphasized. New uses and larger markets in established uses will be vigorously sought.

Research will be continued on the development of new uses, basic properties, and the improvements in mining and processing technology.

Keen competition among lithium producers may result in occasional price reductions in fast-selling lithium compounds. Prices of slower moving lithium metal and compounds also may decrease as consumptions of these materials increase.

Two major producers of lithium chemicals from spodumene are studying the feasibility of recovering various elements including lithium from brines. It is quite possible that one or more new firms may enter the mineral and chemical production fields.

International competition for lithium markets will become more noticeable as the lithium industries in other countries continue to develop.

PROBLEMS

Methods are needed for the efficient recovery and economic disposition of several coproducts and byproducts typically present in lithium-bearing pegmatites to help reduce prices of lithium raw materials.

Reliance on overseas sources for certain lithium minerals (amblygonite, lepidolite, and petalite) could be of concern to the United States if these supplies should become unavailable for any reason. The lack of adequate domestic reserves of these minerals further compounds the problem.

Lithium processing technology is in an early stage of development. Consequently, losses increase the cost of lithium products and adversely affect consumption in certain products, such as lithium hypochlorite as a dry powder bleach and lithium metal in some alloys.

Restrictions on publishing statistical data on the production and consumption of lithium metal, alloys, and compounds and consumption data on lithium raw materials make it difficult for industry and Government to determine requirements, evaluate market potentialities, and plan future action.

Problems of the lithium industry include employment of the production capacities developed to supply the AEC with lithium hydroxide and not needed since 1959, and development of the technology.

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MAGNESIUM AND MAGNESIUM COMPOUNDS

By Lloyd R. Williams [1]

WIDESPREAD deposits of dolomite, an inexhaustible supply of magnesium in sea water, and large deposits of evaporites and well brines provide the United States with abundant resources of magnesium and magnesium compounds. In 1963, well brines, bitterns, and sea water combined with calcined dolomite or lime accounted for more than half of the domestic production of magnesium compounds used as chemicals, fillers or bases in many industrial products including basic refractories. Magnesite was used to produce magnesia. Molding sand has become the principal use for the mineral olivine, which also has been used for refractories.

Dead-burned dolomite accounts for the largest volume production of magnesium compounds and has been produced at a rate of about 2 million tons per year for the past decade. Refractory magnesia production increased at an average of about 8 percent per year during 1959–63 to 713,000 tons in 1963.

In 1963, the United States produced about 49 percent of the world production of primary magnesium but consumed only about 33 percent. West Germany consumed about 25 percent and produced less than 1 percent. The United States ranked first in production and the U.S.S.R. and Norway ranked second and third, respectively. About 90 percent of the total U.S. magnesium productive capacity is in electrolytic plants using magnesium chloride produced from sea water; the remaining 10 percent is in silicothermic processes with dolomite as the primary raw material.

Domestic consumption of magnesium is increasing about 8 percent per year. Use in structural products has not shown any definite trends. A decrease in sand castings has been offset by increased consumption in permanent mold and die castings. Use of primary magnesium in aluminum alloys increased at an average of 10 percent per year from 1959 to 1963 and all other uses increased about 5 percent per year.

In producing magnesia from sea water or well brines calcined dolomite or lime is added to the sea water or brines forming $CaCl_2$ and precipitating $Mg(OH)_2$ which is heated above 3,000° F. to produce MgO. Dead-burned dolomite is produced by heating dolomite above 3,000° F. to drive off the CO_2. Brucite ($Mg(OH)_2$) and magnesite ($MgCO_3$) are similarly treated. In producing the metal from sea water the precipitated $Mg(OH)_2$ is neutralized with HCl to form $MgCl_2$ which is reduced electrolytically to magnesium metal. The chlorine is recovered. In the silicothermic process, calcined dolomite is reduced with silicon in a vacuum retort at 700° F. to 1,000° F. producing magnesium vapor which condenses on cooler surfaces of the retort.

A Materials Survey on Magnesium and Magnesium Compounds published in 1963 reviews the magnesium industry's history, geology, sources, production and uses as well as methods for recovering and processing the element and its many valuable compounds (*5*).[2]

BACKGROUND

Previous to the 19th century limestone rock or dolomite had been found useful to facilitate the production of iron. During the 19th century deposits of natural magnesium carbonate or magnesite were discovered in Moravia, Austria, and Greece. By 1890, after a high temperature basic brick had been made from calcined ore, magnesite was in general use in Europe for refractory linings of Bessemer and open hearth furnaces. In 1913 production of

[1] Commodity specialist.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

magnesia from dolomite began in Pennsylvania.

Previous to World War I, the bulk of world output of magnesite came from Austria-Hungary and Greece. After hostilities started these sources were cut off and in 1917 mining of magnesite deposits was started in California and Washington. At the end of the war a protective tariff placed on crude magnesite discouraged imports from Europe.

By 1928, India began to export caustic-calcined magnesite to the United States. Mining brucite in Nye County, Nev., began in 1929 and in 1937 magnesite mining started in a nearby deposit.

At the outbreak of World War II mining of domestic magnesian ores again expanded for use in the production of refractories and metal. Production of magnesium compounds from ores, brines, and sea water has continued to increase after postwartime adjustments.

Magnesium metal was produced commercially in Germany in 1886 and until World War I most of the world supply of magnesium came from Germany. During the war United States production expanded as foreign sources were cut off. Seven primary magnesium plants were built but at the end of the war, all except two were closed. By 1931, German producers had developed a worldwide market for magnesium and its alloys lasting until World War II.

During 1941–42, to offset the loss of German production and satisfy wartime demands, 16 primary magnesium plants were operating in the United States. Six were silicothermic plants and 10 used electrolytic cells. The peak of U.S. magnesium production was in 1943, 184,000 tons or 62 percent of the world total. By 1946 domestic production had dropped to 6,000 tons, and a plant in Texas was the sole producer. During the Korean war seven government plants were reactivated, but by 1953 all except two of the plants were closed. In 1959 a new silicothermic plant at Selma, Ala., began producing primary magnesium. These three and the Freeport, Tex., plant continue to account for all of the domestic output.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Magnesium Compounds

World production of magnesite in 1963 was estimated at 9 million short tons of which the U.S.S.R. produced an estimated 32 percent and Austria 16 percent. The United States produced 528,000 tons, or 6 percent of the world total.

In 1963, olivine was produced in the United States by several companies in Washington and North Carolina. Northwest Olivine Co. Twin Sisters Quarry in Washington was the major producer. Although brucite was formerly mined in Nevada, no production has been reported since 1959.

In 1963, refractory and caustic calcined magnesia was produced from domestic magnesite in Nevada by Basic, Inc., and refractory magnesia in Washington by Northwest Magnesite Co. Refractory magnesia was made from sea water and calcined dolomite at three plants. The Cape May, N.J., plant obtained dolomite from quarries near Philadelphia, Pa.; that for the Pascagoula, Miss., plant from near Birmingham, Ala.; and that for the Moss Landing, Calif., plant from Natividad, Calif. The latter plant also processed caustic calcined magnesia. At two other plants both refractory and caustic calcined magnesias were produced from sea water; the plant at Port St. Joe, Fla., used oystershell; and the plant at Newark, Calif., sea water bitterns and dolomite with magnesite from Gabbs, Nev. At a plant near Freeport, Tex., refractory magnesia was made from purchased magnesium hydroxide (sea water and oystershell). Near South San Francisco USP grades of magnesium compounds were produced from sea water and dolomite. Magnesium chloride was produced near Freeport, Tex., from sea water and oystershell and magnesium chloride crystals near San Diego, Calif., from sea-water bitterns and dolomite. Magnesium hydroxide is produced at all sea-water plants.

In Michigan near Ludington, Midland, Manistee, and St. Louis various magnesium compounds were prepared from well brines. Precipitated magnesium carbonate was produced at Waukegan, Ill., from dolomite. Magnesium chloride was produced as a byproduct in Delaware, New York, and West Virginia. Small amounts of specified magnesium compounds were produced near Phillipsburg, N.J. Of the 2 million short tons of dead-burned dolomite produced annually in the United States, about half was produced in Ohio. Names, locations, products, and raw materials of plants that produced magnesium compounds in 1963 are shown in table 1.

Magnesium Metal

The United States produced about half and consumed about one-third of the total world production of primary magnesium.

TABLE 1.—*Mines and plants producing magnesite, brucite, and other magnesium compounds in the United States, 1963, by States*

State and company	Location of mine or plant	Products	Raw materials
California:			
Kaiser Aluminum & Chemical Corp. (Refractories Div.).	Moss Landing	Caustic-calcined magnesia; refractory magnesia; magnesium hydroxide; magnesium oxide, extra-light, light and heavy.	Sea water, calcined dolomite.
Do	Natividad	Dead-burned and calcined dolomite	Dolomite.
Marine Magnesium Division, Merck & Co., Inc.	South San Francisco	Magnesium oxides, extra-light, light, and heavy; magnesium hydroxide; precipitated magnesium carbonate; magnesium trisilicate.	Sea water, sea-water bitterns calcined dolomite.
Philadelphia Quartz Co. of California	Alameda County	Epsom salt	Magnesite, brucite, calcined magnesia.
FMC Corp. (formerly Westvaco Chem. Div., Food Machinery and Chemical Corp.).	Newark and San Diego	Caustic-calcined magnesia; refractory magnesia; magnesium chloride crystals; magnesium hydroxide.	Sea-water bitterns, calcined dolomite, magnesite.
Delaware: E. I. du Pont de Nemours & Co., Inc.	New Castle	Magnesium chloride	Byproduct from reducing titanium tetrachloride with magnesium.
Florida: Michigan Chemical Corp	Port St. Joe	Caustic-calcined magnesia; refractory magnesia; magnesium hydroxide.	Sea water, oystershells.
Illinois:			
Johns-Manville Products Corp	Waukegan	Precipitated magnesium carbonate	Dolomite.
Marblehead Lime Co	Thornton	Dead-burned dolomite	Do.
Standard Lime & Cement Co	LaGrange	do	Do.
Michigan:			
The Dow Chemical Co	Ludington	Magnesium chloride crystals; magnesium chloride fluxes; magnesium hydroxide.	Well brines, calcined dolomite.
Do	Midland	Epsom salt; magnesium hydroxide; magnesium oxide, light.	Do.
Harbison-Walker Refractories Co	Ludington	Refractory magnesia	Magnesium hydroxide.
Kaiser Refractories	Midland	Refractory magnesia; periclase	Do.
Michigan Chemical Corp	St. Louis	Precipitated magnesium carbonate; magnesium hydroxide; magnesium oxide, extra-light, light and heavy.	Well brines, calcined dolomite.
Morton Chemical Co	Manistee	Precipitated magnesium carbonate; magnesium oxide, extra-light, light.	Do.
Standard Lime & Cement Co	do	Refractory magnesia	Do.
Mississippi:			
H. K. Porter Co., Inc	Pascagoula	Refractory magnesia	Dolomite, sea water.
Do	do	Dead-burned dolomite	Dolomite.
Missouri: Valley Dolomite Corp	Bonne Terre	Dead-burned dolomite	Dolomite.
Nevada: Basic, Inc	Gabbs	Brucite, magnesite, refractory magnesia, caustic-calcined magnesia.	Magnesite and brucite.
New Jersey:			
J. T. Baker Chemical Co	Phillipsburg	Magnesium chloride crystals, epsom salt; other high-purity magnesium chemicals, magnesium trisilicate.	Magnesium carbonate.
Northwest Magnesite Co	Cape May	Refractory magnesia	Sea water, calcined dolomite
New York: Carborundum Metals Co	Erie	Magnesium chloride	Byproduct from producing zirconium.
North Carolina:			
Balsam Gap Co	Balsam Gap mine (near Sylva).	Olivine	Ore.
Harbison-Walker Refractories Co	Addie mine (near Sylva)	do	Do.
Wiseman Mining Co., Inc	Wray mine (near Burnsville)	do	Do.
Georgia Talc Co	Spruce Pine	do	Do.
Ohio:			
J. E. Baker Co	Millersville	Dead-burned dolomite	Dolomite.
Basic, Inc	Maple Grove	do	Do.
Dolite Co	Gibsonburg	do	Do.
Moores Lime Co	Springfield	do	Do.
Ohio Lime Co	Woodville	do	Do.
Standard Lime & Cement Co	do	do	Do.
Pennsylvania: J. E. Baker Co	York	do	Do.
Texas:			
The Dow Chemical Co	Freeport	Magnesium chloride, caustic-calcined magnesia, magnesium hydroxide.	Sea water, oyster shells.
E. J. Lavino & Co	do	Refractory-grade periclase	Magnesium hydroxide.
Utah: Marblehead Lime Co	Delle	Dead-burned dolomite	Dolomite.
Washington:			
Agro Minerals, Inc	Tonasket	Epsom salt	Lake brine.
Northwest Magnesite Co	Chewelah	Magnesite, caustic-calcined magnesia, refractory magnesia.	Magnesite, ore.
Northwest Olivine Co	Twin Sisters quarry (near Clear Lake).	Olivine	Ore.
Pacific Olivine, Yellow Slide	Clearlake	do	Do.
Scheel Stone Co., Big Slide	Hamilton	do	Do.
Olivine Corp. Whatcom	Bellingham	do	Do.
Omega Mining Inc., Omega	Hamilton	do	Do.
West Virginia:			
Carborundum Metals Co	Parkersburg	Magnesium chloride	Byproduct from producing zirconium.
Standard Lime & Cement Co	Millville	Dead-burned dolomite	Dolomite.

Dow Chemical, the major source of primary magnesium, operates two electrolytic plants in Texas; one at Freeport with a capacity of 55,000 short tons per year, and another at Velasco with a capacity of 37,000 tons. Dow also produces caustic calcined magnesia. Some of the magnesium chloride and magnesium hydroxide processed in an intermediate phase in the production of magnesium from sea water is marketed.

Magnesium also is produced in two silicothermic plants; one with a capacity of 6,200 tons per year is operated by Alabama Metallurgical Corp. at Selma, Ala.; the other with a capacity of 5,000 tons by Chas. Pfizer and Co., Inc., at Caanan, Conn., from dolomite mined near the plant. The last also markets crown magnesium, a magnesium condensate formed in an intermediate stage of the process.

A plant at Henderson, Nev., is capable of producing 12,000 tons of magnesium per year from magnesium chloride, but all of the magnesium recovered at the plant is recycled for titanium production.

Secondary magnesium production was reported from the following plants in 1963: American Smelting & Refining Co., Houston, Tex., and Newark, N.J.; Apex Smelting Co., Chicago, Ill.; and Garfield Alloys, Cleveland, Ohio.

At the close of 1963 about 59 plants in 16 States consumed magnesium for structural products. Eleven plants in California and 11 in Ohio produced castings. In Ohio one also produced forging and another plant produced forgings and extrusions; in Michigan, nine plants produced castings and one produced extrusions; in Illinois, four produced castings, one extrusions, and one sheet and plate; four plants in New York and four in New Jersey produced castings; and in Pennsylvania one plant produced castings, one extrusions, and another forgings. The remaining 11 were scattered throughout the country.

About 140 operations consumed magnesium for distributive or sacrificial purposes, including 82 in making aluminum alloys. Of the 82 plants, 15 are in Ohio; 9 in New York; 7 each in Pennsylvania and Indiana; 6 in Illinois; and 4 each in California, Michigan, New Jersey, and Washington. The remaining 22 consumers of magnesium for aluminum alloys were scattered throughout the country.

DEFINITIONS OF TERMS, GRADES, AND SPECIFICATIONS

Several minerals are used as raw materials for either magnesium metal or compounds production. *Dolomite* (Ca, $Mg(CO_3)$) contains up to about 22 percent magnesia. The term also applies to the rock, dolomite, which is usually a limestone partly transformed to dolomite by hydrothermal alteration. *Magnesite* ($MgCO_3$) has a theoretical magnesia content of 47.6 percent. *Brucite* ($Mg(OH)_2$) contains up to 69 percent magnesia. *Olivine* or *chrysolite* ($(MgFe)_2SiO_4$) is a green to brown mineral used as foundry sand rather than as a source of magnesia. *Magnesia* (MgO) is the product of calcination or thermal decomposition of several magnesium minerals and compounds. *Dead-burned magnesite* is "the granular product obtained by calcining magnesite, or other substances convertible to magnesia upon heating above 2,640° F. long enough to form dense weather-stable granules suitable for use as a refractory or in refractory products" (*1*). Although *periclase* (MgO) occurs as a metamorphic mineral, the term usually applies to a special grade of *dead-burned magnesia* prepared by burning 92 to 98 percent magnesium oxide at about 3,000° F. It has a crystal structure which imparts hardness, chemical stability, and other desirable characteristics. *Calcining* is a heat treatment given to eliminate volatile chemically combined constituents. *Calcined dolomite* is material heated for about 4 hours reaching a final temperature of 2,000° F., thus driving off water and most of the carbon dioxide. *Dead-burned dolomite* is made by burning 0.5-inch size dolomite with an additive of iron oxide in rotary kilns at 3,000° F. to 3,200° F. *Basic refractories* have as major constituents lime, magnesia, or both. Commercial use of this term also includes refractories made of chromite or combinations of chromite and dead-burned magnesite (1). *Brines* are water-base solutions containing dissolved salts. A concentrated brine with sodium chloride (salt) removed is a *bittern*. *Caustic-calcined magnesia* is a reactive magnesium oxide made by calcining magnesium carbonate or magnesium hydroxide at 1,650° F. or lower. It is used in the preparation of oxychloride cement, decoloring agents, rubber, fertilizer, rayon, paper, etc. Specified grades are produced under certain conditions including temperature range and length of time heated. These are designated as extra light, light, and heavy depending on density, chemical purity, reactivity, and grain size.

Specifications for chemical content of primary magnesium set by the American Society for Testing and Materials are as follows:

		Percent
Total of all impurities	Maximum	0.20
Copper	do	.02
Lead	do	.01
Manganese	do	.15
Nickel	do	.001
Tin	do	.01
Other impurities, each	do	.05
Magnesium, by difference	Minimum	99.80

Standards for refractories containing MgO are set by the consumers according to conditions in the furnaces in which they will be used. The American Iron and Steel Institute and the Refractories Institute have published comprehensive data on the properties and uses of basic refractories. Most magnesium compounds are prepared by the producers to meet the specifications set by individual consumers.

ASTM standard designations have been placed on 26 magnesium alloys as shown in table 2. Other magnesium alloys of specific content, required for special applications, are prepared as ordered and priced accordingly.

Temper designations for magnesium alloys cast and wrought, are established by the ASTM, based on sequence of basic treatment. The condition of the designated alloy is noted as follows:

F	As fabricated.
O	Annealed (recrystallized wrought products, only).
H	Strain hardened.
W	Solution.
T	Treated (thermally) to produce strain tempers other than F, O, or H.

Secondary magnesium alloy ingot predominately generated from castings and wrought products is tested to insure the same grades and specifications as the primary alloy with which they are used.

Aluminum is added to magnesium to increase its strength. When manganese is added to magnesium alloys, it increases their resistance to salt-water corrosion. The addition of rare-earth metals to magnesium results in alloys of improved creep strength at elevated temperatures. Zirconium added to magnesium and its alloys results in grain refinement and improved mechanical properties.

TABLE 2.—*Chemical composition of standard magnesium alloy ingot, nominal compositions*

[Percent]

ASTM[1]	Li	Al	Mn	Zn	RE[2]	Zr	Th	Mg
AM100A		10.0	[3] 0.10	[5] 0.3				Balance.
AZ81A		7.6	[3] .13	.7				Do.
AZ31B		3.0	.45	1.0				Do.
AZ61A		6.5	.30	1.0				Do.
AZ63A		6.0	3.15	3.0				Do.
AZ91A		9.0	.20	.7				Do.
AZ91C		8.7	3.13	.7				Do.
AZ92A		9.0	3.13	2.0				Do.
EK30A					[4] 3.0	[5] 0.2		Do.
EK41A					4.0	.6		Do.
EZ33A				2.6	3.2	.7		Do.
HK31A						.7	3.2	Do.
HZ32A				2.1		.7	3.2	Do.
M1A			+ 1.50					Do.
K1A						.6		Do.
ZK60A				5.7		.55		Do.
HM21A			.60					Do.
QE22A					2.1	.7		Do.
ZE10A				1.2	.2			Do.
ZE41A				4.2	1.25	.7		Do.
ZH62A				5.7		.7	1.8	Do.
ZK20A				2.3		.55		Do.
ZK51A				4.6		.7		Do.
ZK61A				6.0		.8		Do.
LA141A	14.0	1.2						Do.

[1] Standard ASTM designation system. Letters represent alloy elements: A, aluminum; E, rare earths; H, thorium; K, zirconium; M, manganese; Z, zinc; and Li, Lithium. A serial letter is arbitrarily assigned (after the numerals) in alphabetical sequence, starting with A and serves to differentiate otherwise identical designations.

[2] Rare-earth elements, usually added as misch metal.

[3] Minimum.

[4] The rare-earth element in this alloy is didymium, essentially 85 percent neodymium and 15 percent praeseodymium. The alloy also contains a nominal 2.5 percent silver.

[5] Maximum.

TECHNOLOGY

Geology

Dolomite, the double carbonate of magnesium and calcium and a sedimentary rock commonly interbedded with limestone, extends over large areas of the United States. Evidence indicated that most dolomites are probably the result of replacement of preexisting limestone beds (*6*).

Magnesite, the natural form of magnesium carbonate, is found in bedded deposits, as deposits in veins, pockets, and shear zones and as replacement bodies in limestone and dolomite. Significant deposits occur in California, Washington, and Nevada. Brucite, the natural form of magnesium hydroxide is found as a decomposition product of magnesium silicates associated with serpentine, dolomite, magnesite, and chromite and in crystalline limestone. A brucite deposit associated with magnesite in Nevada has been mined. Olivine or chrysolite is a magnesium iron silicate usually found in igneous rocks such as basalt and gabbro. It is the principal constituent of a rock known as dunite. Commercial deposits are in Washington, North Carolina, and Georgia.

Evaporites are deposits formed by precipitation of salts from saline solutions. They are found both on the surface and underground. The Carlsbad, New Mexico, and the Great Salt Lake deposits are sources of magnesium compounds. The geological occurrence and chemical composition of inland brines cover a wide range and little information has been published. The only significant commercial source of magnesium compounds from well brines is in Michigan, although brines are known to occur in other areas.

Mining

Open-pit methods are used to mine magnesite and olivine in Washington and North Carolina. Deposits of magnesite and associated brucite at Gabbs, Nev., also have been worked by selective open-pit mining (*21*). The pit design was based on surface mapping and information from diamond drill cores. Mining is controlled by staking mining areas based on assays for lime and silica content obtained from air drill cuttings and entered as isograms on an overlay used in conjunction with a topographic map. Benches 10-foot high are advanced by blasting 12-foot drill holes with ammonium nitrate primed with 60 percent dynamite and detonated with delay electric blasting caps.

Stope and pillar mining using long, ring-drilled blast holes drilled from subdrifts to break the pillar for recovery was used to mine magnesite at Kilmar, Quebec, Canada.

In processing brines to produce magnesium and magnesium compounds consideration is given for discharge of waste water without contamination of water used for other purposes.

Basic Refractories and Magnesium Compounds

Magnesia is the principal product of the magnesium compounds industry. It is obtained from magnesite, sea water, and sea water or well brines combined with dolomite.

Dolomite, magnesite, and brucite ore is delivered from the mines to gyratory or jaw crushers where it is reduced to a minus 5-inch size and carried by belt conveyors to storage piles. The crushed ore is processed according to the manner in which it is to be used. In the case of dolomite, an appreciable quantity of raw, crushed ore is delivered directly to the iron and steel plants. Dead-burned dolomite is obtained by calcining the ore to above 3,000° F. in either blast furnaces or rotary kilns, to drive off CO_2, leaving CaO and MgO. The product is sintered to an extent depending upon the quantity of impurities present.

In the magnesite refractory plants, the minus 5-inch ore is conveyed to cone crushers which reduce it to sizes averaging $\frac{5}{8}$-inch to minus $\frac{3}{8}$-inch, and it is screened and washed. The screens are equipped with washing sprays. The minus $\frac{3}{8}$-inch ore is then passed over rake classifiers to remove slimes, and ground in ball mills to 98 percent minus 100-mesh. The ground discharge from the ball mills is conveyed to flotation cells where a silicate flotation removes talc and serpentine impurities. The cleaned concentrate is dried on a continuous filter and conveyed to the reduction plant.

Magnesite is calcined at temperatures below 1,650° F. to produce caustic calcined magnesia, in which 2 to 10 percent CO_2 is retained. Refractory magnesia is produced from crude magnesite by calcining the ore in rotary kilns at temperatures ranging from 2,640° F. to 3,200° F. Two classes of refractory magnesia are made: Brick, grade and maintenance grade. Periclase is produced when a pure grade of MgO is calcined at temperatures above 3,100° F.

Brucite is beneficiated in a heavy media process for use as refractory material (*10*).

In producing magnesia from sea water or well brines and dolomite, ore containing approximately 22 percent MgO and 30 percent CaO is used. The dolomite is taken from the quarry and crushed in gyratory or jaw crushers, washed, and further reduced in size by ball mills. It is then screened and calcined at temperatures ranging from 1,800° F. to 2,000° F. to drive off carbon dioxide and produce mag-

nesian lime. The magnesian lime is added to sea water to form magnesium hydroxide, the calcium oxide going into solution as calcium chloride. The magnesium hydroxide slurry is filtered to remove water, after which it is conveyed to rotary kilns fired to temperatures that may be as high as 3,360° F. The calcined product containing approximately 97 percent MgO.

When the source of magnesia is sea water or well brine, the waters are treated with calcined dolomite or lime obtained from oystershell by calcining to precipitate the magnesium as magnesium hydroxide. All refractory magnesia obtained from sea water, sea-water bitterns, or well brines is of brick grade.

Commercial grades of magnesium chloride are prepared by combining magnesium hydroxide with hydrochloric acid. The recycling of magnesium chloride resulting from the use of primary magnesium as a reducing agent to produce titanium sponge from $TiCl_4$, is described in the Titanium chapter.

Magnesium sulfate (epsom salts) is produced by dissolving magnesia in sulfuric acid, with subsequent crystallization. When natural epsomite ($MgSO_4 \cdot 7H_2O$) is utilized, it must be cleaned and recrystallized. When the ore is washed, the sulfate dissolves and passes through sieves; the gangue and other impurities remain behind on the sieves. The crystallized powdered magnesium sulfate is washed with water and is packed in conical wooden molds for drying and recrystallization. Various grades of magnesium carbonate are obtained by mixing solutions of magnesium sulfate and sodium carbonate, followed by evaporation.

Magnesium Metal

Two methods are employed to produce magnesium in the United States on a commercial scale: the electrolysis of magnesium chloride obtained from sea water, sometimes referred to as the Dow process, and the thermic reduction of dolomite with ferrosilicon.

In the Dow electrolytic process, sea water is mixed with a slurry of calcium hydroxide. The magnesium in solution in the sea water is precipitated as magnesium hydroxide in large settling tanks or thickeners and is pumped from the bottom of these tanks as a thin slurry containing about 17 percent magnesium hydroxide by weight. Precipitation permits elimination of about 98 percent of the sea water. The magnesium hydroxide slurry is filtered and neutralized with hydrochloric acid to form a 15 percent solution of magnesium chloride. The magnesium chloride solution is evaporated and dehydrated to a solution containing about 48 percent $MgCl_2$, which is mixed with enough dried granular $MgCl_2$ to a consistency of heavy paste and dried in a series of shelf driers to granules containing 74 percent $MgCl_2$. This granular material is fed to the electrolytic cells.

Artificial graphite electrodes are suspended in the bath to serve as anodes. The outer steel shells of the cells, or pots, and their internal baffles, serve as cathodes. Passage of direct current between the pot and electrodes, breaks down the magnesium chloride into chlorine and magnesium. Each cell operates at about 6 volts and 30,000+ amperes. Current efficiency is 75 to 80 percent. Power requirements are approximately 8 to 9 kilowatt-hours per pound of magnesium produced. The magnesium chloride cell feed continuously enters the cell to maintain the correct bath composition and level within the cell.

When the magnesium metal is liberated at the cathode, it rises to the surface of the bath where it is guided by inverted troughs to the metal wells in the front of the cell. This molten metal having a purity of 99.8 percent or more, is dipped from the storage wells into pig forms. The hot chlorine given off at the anode is collected under the tightly closed refractory cell cover and piped to the hydrochloric acid plant (*8*).

In the silicothermic process metallic magnesium is produced in two operations: (1) calcined dolomite and 75-percent-grade ferrosilicon, in ratio of 5 to 1, are mixed, ground heated and briquetted, and (2) the briquettes are charged into tubular retorts, which are heated and evacuated. The magnesium oxide in the calcined dolomite is reduced by the silicon, producing magnesium vapor which is condensed as crystals on a removable condenser that projects from the furnace, and is easily removed. The crystals of 99.98 percent magnesium in the shape of crowns or muffs, are melted and ladled into casting forms.

Other methods of production of magnesium were tried before the close of World War II and abandoned soon thereafter.

Alloying

Usually magnesium is melted and alloyed in open steel pots. Steel does not alloy appreciably with molten magnesium, especially if the bath contains a small quantity of manganese. Because of the chemical reaction of magnesium with the oxygen and nitrogen in the air, it is necessary to cover the molten metal with fluxes which float on top to form a fluid layer or solid crust. Although magnesium will not unite with beryllium to form a binary alloy it will absorb about 0.0005 percent. This small

amount retards oxidation of the molten magnesium.

Fluid flux is heavier than the molten magnesium, and therefore most of it accumulates at the bottom of the container and carries such impurities as MgO with it. A thin film of the fluid covers the top by virtue of its surface tension. The flux which forms a solid crust on top of the molten magnesium is also heavier than the bath but floats on top because it is porous or spongy. Fluid fluxes give better protection to the molten metal, but the solid crust fluxes are easier to separate from the metal during ladling and pouring operations.

Metalworking Techniques

Casting in sand was the first method of forming magnesium alloys. Development of permanent mold and die casting processes followed soon afterward. Casting magnesium alloys in permanent molds instead of sand lowers the cost of production when the number of castings reaches 1,000 pieces. Permanent mold magnesium castings have smoother surfaces and closer dimensions than sand castings. The permanent molds are made of high-carbon gray cast iron. Die casting, which is the process of forcing the molten magnesium alloy into steel dies under pressure, has found favor because of the speed and accuracy of production.

Although magnesium has a hexagonal crystal structure which limits forming at room temperature, it can be readily rolled, extruded, drawn, and forged when it is heated to temperatures ranging from 450° to 700° F.

Magnesium alloys are extruded into many shapes by forcing the solid metal through steel dies. Cast into round billets to fit the cylinder of the extrusion press, the alloy is preheated to 700° to 800° F. and then placed in the cylinder. The press is maintained at a temperature 650° to 850° F., depending upon the alloy to be extruded. Pressures up to 100,000 pounds per square inch are applied to force the alloy through the die.

Pellet extrusion of magnesium alloys is used at the Dow Chemical Co. plant at Madison, Ill. The molten magnesium alloy is poured onto a metal disk spinning at high speed within a large steel tank and hurled in globules or pellets to the inner walls of the tank. Each cooling spherical pellet retains the exact ratio of alloying constituents as the molten mass. As the spherical pellets, about 0.16 inch in diameter, settled to the bottom of the tank, they are transferred to the extrusion press. The extruded sections have extremely fine grain size and high compressive yield strength (*12*).

Magnesium alloys to be rolled into sheet and plate are cast into slabs, the original thickness of which is 3 to 5 inches. They are kept at temperatures of 600° to 850° F., by reheating when necessary, while they are rolled to about ¼-inch thickness, or less. If annealed sheet is required, the hot rolling ceases at about 20 percent above the gage desired, and the metal is annealed for a short time and is cleaned in a solution of acetic or sulfuric acid. The sheet is then cold rolled down to the required gage, after which it is again annealed under heavy cast iron plates to insure flatness.

Magnesium alloy sheet and extrusions are worked in much the same manner as other sheet metals. When it is drawn at 450° to 700° F., according to the alloy, it is possible to accomplish, in a single draw, all that could be done in three operations in steel, brass, or aluminum.

Forging magnesium alloys is accomplished similarly to other metals. Cast forging billets can be used, but an extruded blank is preferred. As in rolling or extrusion, both the metal and the tools are preheated. The forging stock is preheated to 550° to 800° F., according to the composition of the alloy and the design of the forging. Approximately 1 hour is allowed for heating each inch of metal thickness of the blank. Forging dies are usually heated to 400° to 600° F. As in forging other metals, accurate knowledge of metal flow is required in developing die design and blank specifications.

Magnesium and its alloys are the easiest of structural metals to machine, and can be sawed and drilled at room temperature, at greater speeds than most other metals. Magnesium and its alloys can be joined by brazing, riveting, soldering, and adhesive bonding. Primary magnesium and most of its alloys are weldable.

Safety

Before adequate safety measures were adopted, disastrous fires and explosions have resulted in plants that accumulated magnesium dust and drosses, and permitted them to become wetted or exposed to fire. During World War II, the Bureau of Mines provided advice to magnesium producers and consumers for the safe disposal of these waste materials. The care with which magnesium alloy scrap was handled in modern foundries and fabrication plants has been described in detail (*14*). Dust collectors were described, and dust disposal methods were given.

In 1954, when magnesium-thorium alloys were developed, it became necessary for studies to be made of radiation safety in the plants producing and fabricating these alloys, even though radioactivity was comparatively low. Nominal thorium content was 3 percent or less. The Dow Chemical Co. published a bulletin relating its experience with the alloys thus far

and stating that external radiation is not a serious problem when melting and fabricating these alloys. The following precautions should be observed: (1) local exhaust ventilation of areas where the alloys are melted and milled; (2) check regularly air sampling of these areas to determine extent of radiation; and (3) provide adequate local exhaust at the point of welding, to control exposure to radiation.

USES

Magnesium Minerals and Compounds

Dolomite is used in large quantities by the steel industry as a flux and for patching open hearth furnaces. It is an important raw material used in silicothermic magnesium plants and for the production of refractory magnesia and other magnesias from sea water. Large quantities of material which may be classed as dolomite or dolomitic limestone are used widely outside the metallurgical field as a soil conditioner, as an aggregate in concrete, and in road beds. Refractory magnesia and other magnesias are produced from magnesite and brucite. Olivine is used primarily as a molding sand in foundries; its use for the production of refractories has diminished.

The principal uses for magnesium compounds are in the following industries:

Compound and grade	*Use*
Magnesium oxide:	
Refractory grades.	Basic refractories.
Caustic-calcined	Cement, rayon, fertilizer, insulation, magnesium, metal, rubber, fluxes, refractories, chemical processing and manufacturing, uranium processing, paper processing.
U.S.P. and technical grades.	Rayon, rubber (filler and catalyst), refractories, medicines, uranium processing, fertilizer, electrical insulation, neoprene compounds and other chemicals, cement.
Precipitated magnesium carbonate.	Insulation, rubber, pigments and paint, glass, ink, ceramics, chemicals, fertilizers.
Magnesium hydroxide	Sugar refining, magnesium oxide, pharmaceuticals.
Magnesium chloride	Magnesium metal, cement, ceramics, textiles, paper, chemicals.

Basic refractories used in metallurgical furnaces are produced from magnesium oxide. Technological advances in steel production required higher temperatures which were met by refractories manufactured from high purity magnesia capable of withstanding temperatures above 3,500° F.

Magnesia is used as a stabilizing or vulcanizing agent in rubber. The high electrical resistance of fused magnesia or periclase makes it useful as an insulator in electric furnaces and domestic appliances. Magnesia serves as an absorbent and catalyst in the carbonate leach circuits for the recovery of uranium oxide from uranium ores.

Basic magnesium carbonate is used as a thermal insulator for boilers, pipes, etc.; in table salt to prevent caking; and in preparation of pharmaceuticals and cosmetics. Magnesium chloride derived from sea water is primarily used for the production of magnesium metal. Small quantities derived from sea water and well brines are used in industrial chemicals and oxychloride cement for flooring. Magnesium sulfate is used for pharmaceuticals, dyes, sizing, paper manufacture, fertilizers, explosives, and matches.

Magnesium and Magnesium Alloys

During 1959–63 magnesium used as a constituent of aluminum alloys amounted to about 40 percent of the total magnesium used and magnesium alloys consumed another 40 percent. Magnesium alloys are used in aircraft engines and in airframe structures, wings, undercarriages, floor beams and plates, skins, and wheels. In helicopters, applications of magnesium alloys include extrusions, sheet, castings, forgings, bars, and tubes. Magnesium alloys are used in jet engines and guided missiles (*13*). The lightweight magnesium metal has replaced heavier metals used for many parts of automotive and transportation equipment.

Other uses for magnesium were as a reducing agent for titanium, zirconium, hafnium, uranium, and beryllium; and as a scavenger and deoxidizer. Magnesium anodes are standard equipment for the cathodic protection of iron and steel, particularly in underground pipe, ships, and water tanks.

Trends of uses of primary magnesium for structural materials during 1961–63 are shown in table 3.

TABLE 3.—*End uses of primary magnesium in structural products*

[Percent]

Product	1961	1962	1963
Aircraft and missiles	49	32	30
Consumer products	14	17	18
Electrical and electronic equipment	9	15	15
Machinery and tools	11	16	17
Materials handling equipment	6	6	6
Surface vehicles	7	10	10
Graphic arts	2	2	2
Miscellaneous	2	2	2

ALTERNATE MATERIALS

Refractories are made from many materials including bauxite, alumina, zirconia, mullite, silicon carbide, and boron carbide. Depending upon requirements, many of these may be used in place of magnesia refractories.

Aluminum can be used in most structural applications where magnesium is now used.

Sodium also is used to reduce titanium tetrachloride to produce titanium metal.

SECONDARY SOURCES AND RECOVERY OF MAGNESIUM

Secondary magnesium is obtained from two general sources: New scrap and old scrap. New scrap is generated in sheet mills and fabricating plants. It consists of clippings, turnings, borings, skimmings, slags, drosses, and defective articles rejected by the manufacturer or returned to him unused. Old scrap is metal contained in articles that have been discarded because of wear, damage, or obsolescence, usually after they have served a useful purpose. Typical sources of old magnesium scrap are wrecked aircraft, old and obsolete mobile equipment, and lithographers' plates.

RESERVES

Magnesium and magnesium compounds are produced from the following four raw material sources: (1) sea water, (2) dolomite, (3) ores other than dolomite, and (4) evaporite deposits and lake and well brines. Sea water with a magnesium content of 0.13 weight-percent is an inexhaustible resource.

Large deposits of dolomitic limestone and dolomite are widely distributed throughout the world. Four major dolomite areas are in the following areas of the United States: (1) Appalachian Valley region extending from Vermont through Massachusetts, Connecticut, New York, New Jersey, Pennsylvania, Maryland, Virginia, Tennessee, Georgia, and Alabama; (2) western Ohio and eastern Indiana; (3) a U-shaped belt starting in southeastern Minnesota and extending through northeastern Iowa, northern Illinois, southern and eastern Wisconsin and across upper Michigan along the north shores of Lakes Michigan and Huron; and (4) southern Missouri and northern Arkansas. In the West widespread deposits of high-magnesium limestones are reported in central and southern New Mexico. Discontinuous masses of dolomite occur throughout central and southern California and southwestern Arizona. Large quantities of dolomite are available in Texas, Oklahoma, Colorado, Utah, Wyoming, Montana, and northeastern Washington.

The principal magnesium ores other than dolomite are magnesite, brucite, and olivine (chrysolite). Magnesite is the most plentiful of these. Estimated data on world magnesite reserve of 8.3 billion tons, shown in table 4, do not include all deposits. Large deposits also occur in Spain, Austria, Yugoslavia, Pakistan, and Sudan. Deposits estimated at less than 1 million tons were reported in Mexico, Iran, Philippines, Australia, United Arab Republic (Egypt), and Republic of South Africa. Small deposits have been noted in Cuba, Sweden, Norway, Poland, Scotland, France, Italy, Kenya, and Tanzania (*5*).

TABLE 4.—*World magnesite reserves*

Country	Million tons	Country	Million tons
China	5,000	United States	65
Korea, North	2,000	Brazil[1]	7
New Zealand	600	Venezuela	3
U.S.S.R.	400	Greece	1
Czechoslovakia	100	Turkey	1
India	100	Canada	1

[1] Per meter of depth (average depth not known).

The reported estimate of 65 million tons of magnesite reserves and resources in the United States is divided as follows: 88 percent in Nevada including 27 million tons of magnesite containing less than 5 percent MgO; 11 percent in Washington; and the remaining 1 percent in California (*6*). Magnesite also occurs in Texas, New Mexico, Idaho, Utah, Pennsylvania, Massachusetts, Maryland, New Jersey, and New York, but reserves have not been estimated in these States.

Brucite reserves are estimated to total 3 million tons in Nevada, and 2 million tons in North Korea. The mineral also is found in Arizona and in the United Kingdom, Ireland, and Canada.

The reserve of olivine is estimated at 230 million tons averaging 48 percent magnesia in North Carolina and Georgia (*10*).

In Washington the olivine reserve in the form of dunite is estimated at 50 million tons on Cypress Island and many million tons in the Twin Sisters Region (*9*).

Reserves of magnesium salts obtained as brines from underground evaporite deposits are difficult to estimate. Available information on magnesium salts in surface evaporites is insufficient to estimate reserves. A preliminary survey in 1950 indicated 13 million tons of MgO equivalent in brines in Saskatchewan, Canada.

SOURCES OF STATISTICAL INFORMATION

In addition to its annual canvasses of production, sales, and use of magnesium and magnesium compounds in the United States, the Bureau of Mines gathers monthly statistical information covering domestic production, stocks, and shipments of primary magnesium.

Export-import figures covering magnesium, crude magnesite, and magnesia, are taken from the information gathered by the Bureau of Census, Department of Commerce. Information concerning production of magnesium and magnesite ore in foreign countries, is accumulated by the Bureau of Mines from published sources and reports by mineral attaché at foreign offices.

PRODUCTION, CONSUMPTION, AND TRADE

Magnesium Ores and Compounds

Statistical data from foreign countries on production of magnesium ores and compounds are limited to crude magnesite. Table 5 shows a comparison of crude magnesite production in the United States with total world production. Although the world growth rate is about 11 percent per year, magnesite production in the United States showed little overall change during the past decade. Table 6 presents data on magnesia sold or used by producers. Data in table 7, give exports and imports of magnesium compounds. Imports are principally crude and calcined magnesite.

In 1963, about 74 percent of the caustic calcined and refractory magnesia sold or used came from well brines, bitterns, and sea water using calcined dolomite or lime in the process. The remaining 26 percent was from magnesite. About 2 million tons of dead-burned dolomite used for refractories and flux was produced from dolomite.

TABLE 5.—*Magnesite production*

[Thousand short tons]

Year	World	United States
1954–58 (average)	5,150	526
1959	6,100	594
1960	6,850	499
1961	8,300	604
1962	8,600	492
1963	9,050	528

TABLE 6.—*Magnesia sold or used by producers in the United States*

[Thousand short tons]

Year	From magnesite, brucite, and dolomite		From well brines, and sea-water bitterns[1]		Total
	Caustic-calcined	Refractory	Caustic-calcined	Refractory	
1959	16	176	38	342	572
1960	20	148	46	358	572
1961	23	161	57	438	679
1962	21	135	65	441	662
1963	70	149	65	564	848

[1] Includes dolomite used in process.

TABLE 7.—*Magnesia and other magnesium compounds imported and exported*

[Thousand short tons and thousand dollars]

Year	Imports		Exports	
	Quantity	Value	Quantity[1]	Value
1954–58 (average)	100	$5,799	47	$2,529
1959	171	10,434	97	5,828
1960	134	8,334	101	6,674
1961	72	4,357	130	8,522
1962	122	6,527	78	5,790
1963	110	5,588	87	6,298

[1] Chiefly magnesite and dead-burned magnesia. Includes estimate of small quantities of other magnesium compounds.

Magnesium

During World War II, the United States became the leading magnesium producing country. Since 1952 exports have exceeded imports. Statistics for consumption of magnesium in foreign countries are not available.

Data in table 8 show a steady increase in United States production of primary magnesium, and data in table 9 show domestic consumption and producers and consumers stocks of the primary metal. Industry reports indicated that exports of primary magnesium exceeded 10,000 tons in 1963. Of the world total production of 155,000 tons, West Germany imported about 25 percent.

In 1960, Furukawa Magnesium Co., Ltd. expanded its silicothermic plant at Oyama, Japan, to increase annual magnesium capacity from 2,000 to 4,500 tons. Dominion Magnesium, Ltd., of Canada expanded its silicothermic plant capacity from 8,000 to 10,000 tons per year in 1961. The Norsk-Hydro-Elektrisk A/S expanded its plant at Herya, Norway, to an annual capacity of 19,000 tons in 1962. In 1963, a 5,000-ton capacity thermal reduction plant was erected at Hopton, England, by Magnesium Elektron, Ltd.

The U.S. tariff rates for magnesium and magnesium compounds are shown in table 10.

TABLE 8.—*Primary magnesium production*

[Thousand short tons]

Year	World	United States
1954–58 (average)	116	62
1959	82	31
1960	103	40
1961	116	41
1962	146	69
1963	155	76

TABLE 9.—*Domestic consumption and imports for consumption of primary magnesium (ingot equivalent and magnesium content of magnesium base alloys)*

[Short tons]

Year	Consumption				Imports for consumption
	Structural products	Used in aluminum alloys	Nonstructural purposes except aluminum alloys	Total	
1954–58 (average)	18,745	10,894	14,178	43,817	969
1959	18,638	14,780	8,133	41,551	645
1960	12,419	12,511	12,170	37,100	433
1961	13,391	19,754	12,388	45,533	1,041
1962	21,032	18,405	7,883	47,320	2,447
1963	19,500	21,780	9,960	51,240	2,374

TABLE 10.—*Tariff schedules of the United States*

Item	TSUS No.	Rate of duty, Aug. 31, 1963	Statutory rate of duty
Magnesite:			
Crude	522.61	$5.25 per ton	$10.50 per ton.
Caustic calcined	522.64	$10.50 per ton	$21.00 per ton.
Refractory magnesia (including dead-burned magnesite, fused magnesite, and dead-burned dolomite):			
Less than 4 percent lime	531.01	0.38¢ per pound	0.75¢ per pound.
More than 4 percent lime	531.04	12 percent ad valorem	30 percent ad valorem.
Magnesium compounds:			
Carbonate, unprecipitated	419.20	8.5 percent ad valorem	25 percent ad valorem.
Carbonate, precipitated	419.22	0.35¢ per pound	$1.50 per pound.
Chloride, anhydrous	419.24	1¢ per pound	1¢ per pound.
Chloride, other	419.28	0.42¢ per pound	0.625¢ per pound.
Oxide, calcined	419.32	2¢ per pound	7¢ per pound.
Epsom salts	419.34	0.375¢ per pound	0.75¢ per pound.
Magnesium: unwrought other than alloys, waste and scrap.[1]	628.55	40 percent ad valorem	100 percent ad valorem.
Magnesium alloys:			
Unwrought	628.57	16¢ per pound contained magnesium +8 percent ad valorem.	40¢ per pound contained magnesium +20 percent ad valorem.
Wrought	628.59	13.5¢ per pound contained magnesium +7 percent ad valorem.	40¢ per pound contained magnesium +20 percent ad valorem.

[1] Duty on waste and scrap temporarily suspended as provided by Public Law 88-324, effective July 1, 1964.

STRATEGIC CONSIDERATIONS AND GOVERNMENT PROGRAMS

In addition to deposits of magnesite, olivine, and evaporites the wide distribution and large deposits of dolomite and development of plants using the virtually limitless supply of magnesium in sea water assure self-sufficiency for the United States of magnesium and magnesium compounds including refractory magnesia.

On June 30, 1964, government inventories totaled 173,500 short tons of specification grade and 54 tons of subspecification grade magnesium in the national (strategic) stockpile.

There are no current government programs concerning magnesium.

PRICES

The price per pound of primary magnesium has declined from $1.83 in 1918 to become steady at 20.5 cents from 1943 to 1950. Three increases in 1950 brought the price to 24.5 cents in September. In January 1951, the Government's General Ceiling Price Regulation fixed the price at 24.5 cents. In 1953, the price was raised to 27 cents, and remained at that point throughout 1954. Gradual increases during 1955 and 1956, resulting from the rise in cost of fuel, raw materials, transportation, and labor, brought the price of primary magnesium to 35.25 cents a pound in 1956. It has remained at this price in the United States.

The average prices paid for dead-burned dolomite and magnesium oxide during 1959–63 are shown in table 11.

TABLE 11.—*Average values per short ton of principal magnesium compounds in the United States*

Year	Dead-burned dolomite	Crude magnesite	Caustic-calcined magnesia	Refractory magnesia
1954–58 (average)	$15.46	$4.66	$60.14	$52.77
1959	16.63	4.05	65.43	60.73
1960	16.66	4.11	65.03	60.99
1961	16.40	5.14	62.55	59.11
1962	16.73	4.65	62.27	61.09
1963	16.96	3.37	58.26	62.24

TAXES

Depletion allowance for deposits of magnesite, dolomite, and brucite in the United States was 15 percent, and for olivine, 23 percent.

RESEARCH

Research by industry, government, and educational institutions in production and use of magnesium and magnesium compounds has progressed steadily since World War II.

Investigations in the laboratories of Metal Hydrides, Inc., Beverly, Mass., has provided information on the use of magnesium powder as solid fuel in missiles. Harbison-Walker Refractories Co. has a research center near Pittsburgh, Pa., and Kaiser Refractories Division operates research facilities at Milpitas, Calif. The latter two companies developed methods to produce high-purity magnesia for the manufacture of high-temperature refractories, to meet the requirements of the basic oxygen furnace.

Research for the development of refractories to withstand temperatures up to 4,000° F. is continuing. Magnesium oxide ceramic material with a purity of 99.95 percent MgO is available for crucibles that will withstand temperatures as high as 5,000° F.

Much work was done on the relationship of the melting temperature of the bonding material in the refractory to the strength of the refractory. High-purity magnesite either alone or in combination with other high-purity minerals produced better grade refractories than less pure magnesite.

FMC Corp. does research at chemical laboratories in Newark, Calif., to develop specific types and grades of magnesia products (*5*).

Dow Chemical Co. developed processes for recovery of magnesium compounds from deep-well brines in Michigan. The company developed the "bath-tub" cell for electrolysis of magnesium chloride to produce magnesium. Research on the feed, amperage, and design of the electrolytic cell is continuing to improve its efficiency.

Technologic research for the production of high-strength premium quality magnesium castings led to the development of alloy systems and improved casting design and techniques (*9*). Alloys in the magnesium-aluminum-zinc system were useful up to 550° F.; and those in the magnesium-thorium-zirconium system were useful up to 650° F. A comparatively new alloy containing lithium was developed (LA 141A), with a specific gravity of 1.35 (*17*).

The Bureau of Mines does research to provide safer and more efficient methods of mining and mineral processing. This work includes fundamental studies of magnesium alloys and recovery of the metal and its alloying ingredients from scrap (*3*). The Bureau measured the vibration-damping capacity of magnesium alloys in missiles and space vehicles subject to vibration stresses and provided fundamental information on the lightweight magnesium-lithium series of alloys (*17*, *20*).

OUTLOOK

Ores such as dolomite, magnesite, brucite, and olivine should continue as the principal world source of refractory magnesium oxide. However, the refractory industry is expected to require increasing quantities of high-purity magnesium oxide such as that which can be made from sea water and dolomite and various brine solutions.

Dead-burned dolomite accounted for the largest volume production of magnesium compounds. Use of dolomite covers a comparatively wide field and the outlook is based primarily on consumption records that show little change during the past decade. There is no outstanding new use for dead-burned dolomite. Future production will probably continue to average about 2 million tons per year.

Increased knowledge of the advantages of high-purity magnesium oxide used for basic refractories will lead to increased production of magnesia. Using this assumption and relying upon the record of the past decade the consumption of magnesium oxide for refractories will increase 7 to 8 percent per year and will reach 1.2 million tons in 1970 and 2.5 million tons in 1980.

Although electrolytic processes using sea water will continue to be the predominate method for making magnesium metal, thermal reduction plants also will be built in areas with high cost electric energy.

Magnesium consumption from 1961 to 1963 inclusive, together with increased interest in better casting techniques, indicates a 4- to 6-percent increase in consumption per year; consumption in 1970 is projected to about 27,000 tons of magnesium for structural products and will reach 43,000 tons in 1980.

Based on records of past consumption and anticipated demand, magnesium consumption for use in aluminum alloys is estimated to increase 9 to 10 percent per year amounting to a projected consumption of 43,000 tons of magnesium in 1970 and 100,000 tons in 1980.

Estimates of future titanium production show that consumption of magnesium as a reducing agent for titanium will increase about 10 percent per year amounting to a projected consumption of 5,000 tons in 1970 and 12,000 tons in 1980.

Past consumption records of magnesium for other uses indicate an increase of about 4 percent per year, amounting to a projected consumption of 10,000 tons in 1970 and 15,000 tons in 1980.

The total consumption of magnesium in the United States is expected to increase 7 to 8 percent per year and reach 85,000 short tons in 1970 and 170,000 tons in 1980.

This growth rate may be increased substantially if marketing practices are intensified, research and development are increased, and new plants planned in 1963 are constructed.

Harvey Aluminum, Inc., and Standard Magnesium and Chemical Co. (a division of Kaiser Aluminum and Chemical Corp.) announced plans to build primary magnesium plants in the Pacific Northwest—a 20,000-ton-per-year plant and a 10,000-ton-per-year plant, respectively.

PROBLEMS

The magnesium metal industry in the United States is confronted with the basic problem of expanding markets to fully utilize available productive capacity and vast resources.

An important problem is the lack of understanding by prospective consumers of the advantages of magnesium over other lightweight materials. A special problem is the unfounded apprehension that all forms of magnesium are fire hazards, a belief acquired when it was used extensively for flares and other pyrotechnics in wartime.

There is a need for improving the technology of primary metal production and secondary recovery. The present continuous process of electrolysis of magnesium chloride requires large expenditures for electric energy, and uses magnesium chloride, a material that is difficult to handle, for cell feed. The silicothermic method is a batch process with the high labor requirements inherent in such operations, and special care is required in operating the retorts to prevent burning of the magnesium.

The use of magnesium alloys as structural materials has been restricted because of their low strength at elevated temperatures, limited resistance to galvanic and stress corrosion, and the high cost of magnesium, relative to competing materials. In 1963, only about 30 magnesium alloys had been developed, and the range of their properties fell short of that needed for wide use of the metal commensurate with its potential lightweight applications. Accurate physical, metallurgical and corrosion data on many potentially useful magnesium alloys are lacking.

More intricate machinery is used to manufacture magnesium die cast parts than aluminum parts. Consequently, magnesium has not been fully utilized in many consumer-oriented products such as sporting goods, hand and motor operated household and garden tools, and business machines where lightness and superior dampening properties of the metal would be advantageous. Manufacturers of castings need more information on casting techniques to produce good magnesium castings.

Incomplete knowledge of worldwide resources and industry activities continues to be a problem in evaluating sources of supply, determining requirements, and planning future programs.

Future expansion of installations for producing refractory magnesia from sea water is faced with the problem of selecting plant sites adjacent to sea water and close to an adequate supply of suitable dolomite. Although refractory bricks, made from magnesia produced from sea water and dolomite and containing 98 percent MgO, stand tests under 25-pound load at 3,500° F., there remain problems of meeting specifications for diversification of requirements which include reducing the silica and calcium carbonate to lower percentages enabling production of a brick that will withstand temperatures up to 5,000° F.

High-temperature refractories made from high-purity magnesia raise the problem of finding methods to lower the firing temperature in making the product and still maintain a periclase to periclase bonding.

Expansion of the export markets for magnesia refractories is retarded by high foreign tariffs.

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MANGANESE

By Gilbert L. DeHuff [1]

THE PRINCIPAL use of manganese is in producing steel, chiefly to counteract the effects of sulfur. It is also used to impart strength, toughness, hardness, and hardenability to some steels. Moreover, manganese has beneficial deoxidizing effects, although it is not primarily used for this purpose. For these applications, manganese usually is introduced in the form of ferromanganese. Manganese dioxide ores have important uses in manufacturing manganese chemicals, as an oxidizing agent, and as a depolarizing agent in dry-cell batteries. Electrolytic manganese is a satisfactory form to introduce manganese to metallurgical or chemical operations where impurities are particularly objectionable.

Manganese ore is classified according to category of use into the following three general grades: Metallurgical, battery, and chemical, including miscellaneous.

The world reserve of manganese ores of varying grades is estimated to exceed 2 billion tons, the largest deposits being in U.S.S.R., Gabon, Republic of South Africa, Brazil, India, and China. The Gabon reserves include battery-grade ore. The manganese ore reserve in the United States from which a concentrate containing 35-plus percent manganese can be obtained by ordinary means of concentration is roughly 1 million tons, largely dependent on premium prices. In addition, large domestic manganese resources occur as low-grade and refractory deposits in Aroostook County, Maine, the Cuyuna range Minnesota, Chamberlain, S. Dak., Batesville, Ark., and the Artillery Mountains, Ariz.

In the period following the Korean war, with premium Government prices, U.S. production of manganese ore was about 15 percent or less of its requirements, most of the production going to Government stockpiles. By 1963, U.S. production had dropped to a negligible quantity in terms of consumption. Because of the strategic importance of manganese, the Federal Government has been greatly interested in assuring an adequate supply. It has established substantial stocks of ore, ferromanganese, and metal; has investigated virtually every known manganese occurrence in the United States; has financed important new production at home and abroad; and has devoted much energy and financial support to research. This research developed silicomanganese and electrolytic manganese to the point of commercial production and application; led to the commercial production of high-purity synthetic manganese dioxide from low-grade domestic manganiferous materials; and demonstrated the technical feasibility of several processes for utilizing the large domestic manganese resources.

There remains no satisfactory substitute for manganese in its major metallurgical uses, and the problems of stockpiling—the optimum quantity and best type of material—continue to demand consideration.

BACKGROUND

Manganese oxide was used by the ancient Egyptians and Romans for controlling the color of glass. This application for glass and pottery constituted the principal commercial use for manganese until the latter part of the 18th century. From then until about 1855, manganese ores were used extensively in the manufacture of chlorine (*19*).[2] The use of umber as a drier for oils appears to date from the middle of the 17th century (*10*). The first recorded mining of manganese ore in the United States was in 1837 in Hickham County, Tenn., apparently for the purpose of coloring earthenware. The use of

[1] Commodity specialist.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

manganese in manufacturing iron and steel dates from 1839, when Heath demonstrated that it improved malleability of the product (*19*).

In 1856 the Bessemer process for making steel was initiated but the product was not satisfactory because it could not be forged or hot rolled without cracking or tearing. Shortly afterwards, Robert Mushet discovered this failing could be overcome by the introduction of manganese in the form of spiegeleisen. Since then, manganese has been necessary to the commercial production of steel in the various production methods which have developed since Bessemer's discovery.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Minable manganese ore deposits have worldwide distribution, and many countries are substantial producers. The principal producing countries are the U.S.S.R., Republic of South Africa, Brazil, India, China, Gabon. Total manganese ore production in 1963 was estimated at 16 million tons, compared to an estimated world iron ore production of 510 million tons for the same year.

Since the close in 1961 of the emergency-generated operations of Manganese, Inc., at Henderson, Nev., the only manganese ore (35 percent or more manganese) producing industry in the United States has consisted of the production in Montana of manganese oxide nodules by The Anaconda Company from stockpiled Montana carbonate ore and the production of battery ore by Taylor-Knapp Co. at Philipsburg, Mont., together with some production of metallurgical ore in Socorro County, N. Mex., and in 1962 in southern California. In 1963, New Mexico's production exceeded that of Montana. Total U.S. production for 1963 was only 11,000 short tons, whereas domestic consumption was 1.8 million tons.

The United States and the U.S.S.R. are the principal manganese-ore-consuming countries, the former using ore chiefly for the production of manganese ferroalloys and the latter for the production of pig iron as well as of alloys. The large steel-producing countries of continental Europe, the United Kingdom, and Japan, are consumers of lesser importance by their production of manganese ferroalloys. The Republic of South Africa and Japan, as well as the United States, produce electrolytic manganese metal for export. The Republic of South Africa and India, together with other ore-producing countries, have become ferromanganese producers of some consequence.

Most of the manganese ferroalloys and metal used in the United States are consumed by the iron and steel industry. The nonferrous, dry-cell battery, chemical and miscellaneous industries consume only a small quantity. Except for The Anaconda Company, which has been a domestic producer of ferromanganese as well as of high-grade metallurgical ore in the form of nodules, the U.S. manganese-ore-producing industry has not been integrated with the ore-consuming industries. The principal producers of manganese ferroalloys, Bethlehem Steel Co., United States Steel Corp., and Union Carbide Corp., however, have substantial investment in important foreign manganese-mining operations, and the two steel companies are large alloy consumers. E. J. Lavino & Co. holds a significant position as a producer of ferromanganese and an importer of manganese ore. In all, approximately a dozen companies produce ferromanganese, silicomanganese, or spiegeleisen in the United States, and the greater part of this production comes from plants east of the Mississippi River. Three companies, American Potash & Chemical Corp., Foote Mineral Co., and Union Carbide Corp., produce electrolytic manganese metal.

Manufacturers of dry-cell batteries and certain manufacturers of chemicals, and users of dioxide ore for other chemical purposes, constitute separate segments of the traditional domestic manganese-ore consuming industry. Most are in the eastern United States.

Manganese ores and products are imported into the United States by some of the large consumers, either directly or through agents, and by importer-dealers, traders, or brokers. In the United States, these importing and trading firms have offices principally in New York and Philadelphia. A number of these particular firms are subsidiaries or affiliates of houses headquartered in London or Europe. Actual import of ores is largely through Baltimore, Md., Philadelphia, Pa., Virginia, and gulf coast ports.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

In its statistical presentations, the Bureau of Mines has for many years used the term *manganese ore* for those ores containing 35 percent or more manganese; *ferruginous manganese ore* for those containing 10 to 35 percent manganese; and *manganiferous iron ore* for those containing 5 to 10 percent manganese. In each instance, the material reported as ore may actually have been concentrate, nodules, or a synthetic ore. In the two lower grades, particularly that of the ferruginous

manganese ore, ores may be included which do not have sufficient iron content to allow them to qualify technically as ferruginous or iron ore. These are matters of expediency that avoid unwieldy and unnecessary detail in the tabulation of statistics, and avoid difficulties as to publication, confidentiality, and practical use of data which arise from too narrow classification. The general term *manganiferous ore* may be used statistically by the Bureau to include any ore of importance for its manganese content containing less than 35 percent manganese but not less than 5 percent. The industry, however, may go as low as 2 percent manganese in its use of the modifier "manganiferous."

In this chapter, unless otherwise qualified, *manganese ore* will be used to mean ore containing 35 percent or more manganese, and may include concentrate, nodules, or synthetic ore. The term *synthetic ore*, as used in this chapter and to date in the Bureau's statistics, refers to material that is the equivalent of, or better than, natural ore, which can be put to the same uses, and is produced by means other than ordinary concentration, calcining, sintering, or nodulizing. The most important use of the term "synthetic ore" has been to label manganese dioxide produced chemically or electrolytically for use in the manufacture of dry-cell batteries.

Manganese ore, and to a lesser extent the lower grade manganiferous ores, falls into three general classifications determined largely by adaptability to the three principal categories of use—metallurgical, battery, and chemical (including miscellaneous or associated industries). In the Bureau's statistics, this is recognized by classifying the various ores as metallurgical, battery, or miscellaneous. The determining factor is suitability of ore for use by the iron-steel-ferroalloy industry, or by the battery industry.

For the national stockpile specifications essentially three major grades of ore have been established—metallurgical, battery, and chemical. The chemical-grade is not otherwise recognized by the industry, although it is based primarily on industry requirements for the manufacture of potassium permanganate and for use as an oxidizing agent in chemical processes such as the manufacture of hydroquinone.

National Stockpile Specification P–30–R, Manganese—Metallurgical, January 8, 1953, covered ore, nodules, and sinter "suitable for the manufacture of commercial grades of ferromanganese and special manganese alloys, and for the production of chemicals which do not require ore of high manganese dioxide content." The chemical requirements, for it and for the March 14, 1958 revision, P–30–R1, were essentially as follows:

		Percent by weight (dry basis)			
		P–30–R [1]	P–30–R1 [2]	P–30–R [3]	P–30–R1 [4]
Manganese	Minimum	46.00	46.00	40.00	44.00
Iron	Maximum	8.00	8.00	16.00	12.00
Silica-plus-alumina	do	12.00	12.00	([5])	15.00
Phosphorus	do	.18	.18	.30	.24
Copper	do			.25	
Copper-plus-lead-plus-zinc	do	.10	.20	1.00	.30

[1] Any proposal could be rejected if its guaranteed chemical analysis on the weighted average basis were inferior.
[2] Material purchased "shall conform" on a weighted average basis for each contract.
[3] No proposals considered unless guaranteed chemical analysis on the weighted average basis is equal or better.
[4] Each lot delivered "shall conform", a lot being "any quantity determined by the Government to require a separate chemical analysis report."
[5] "No limit specified for material, which may be offered; however, material over 15 percent will be purchased in exceptional cases only."

National Stockpile Specification P–29–R3, Manganese Dioxide—Battery Grade, June 16, 1961, "covers manganese dioxides in the form of synthetics, ores, or concentrates, suitable for use in the manufacture of dry-cell batteries." Although two grades, military (Grade A) and commercial (Grade B), are recognized for both synthetic and natural manganese dioxide, only the two natural grades and the military grade of synthetic are provided for in P–29–R3. Suitability for the manufacture of satisfactory batteries is in reality the minimum controlling specification for the three grades of P–29–R3. Available oxygen as percent minimum MnO_2 is set by this stockpile specification as 85.0 for Synthetic Grade A, 75.0 for Natural Grade A, and 68.0 for Natural Grade B.

National Stockpile Specification P–81–R, Manganese Ore—Chemical Grade, October 28, 1957, recognizes two types:

"Type A shall be satisfactory for use as an oxidizing agent in chemical processes, such as in the manufacture of hydroquinone.

"Type B shall be satisfactory for use in the production of potassium permanganate and other permanganate chemicals."

The chemical requirements for Type A follow:

Type A	*Percent by weight (dry basis)*
Manganese dioxide (minimum)	80.0
Iron (maximum)	3.0

In addition, "Final acceptance of Type A material shall be based upon the results of evaluation tests by the purchaser, or his designee, to determine its suitability as an oxidizing agent in chemical processes such as in the manufacture of hydroquinone." Specification P–81–R dropped the requirement of immediately pre-

ceding Specification P–81 (18 April 1950) that upon X-ray examination there shall be evidence of the predominance of pyrolusite.

The chemical requirements for Type B for P–81–R and the immediately preceding P–81 are:

Type B		Percent by weight (dry basis)	
		P–81	P–81–R
Manganese dioxide	Minimum	85.0	82.0
Managanese	do		53.0
Iron	Maximum	3.0	3.0
Silica	do	3.0	5.0
Alumina	do	3.0	3.0
Phosphorus	do	.10	.20
Arsenic	do	.05	.10

Commercially, all manganese ores are purchased by negotiation. Although the national stockpile specifications represent the grade of ores desired by industry, the practice of blending ores, adapting particular ores to special conditions of operation, supply, use or price, permits considerable room for negotiation and explains the lack of standard industry specifications. The specifications of one company will differ from those of another, and the specifications of a particular company will change with the passage of time. When the supply of ore is plentiful, specifications are more severe than when ore is scarce.

National Stockpile Specification P–30a–R2, Ferromanganese (Standard High-Carbon), July 26, 1961, "covers standard high-carbon ferromanganese suitable for use in the production of iron and steel." Its chemical requirements are as follows:

	Percent by weight
Manganese	74.00 to 77.50
Carbon (maximum)	7.50
Silicon (maximum)	1.00
Phosphorus (maximum)	.35
Arsenic (maximum)	.20
Phosphorus plus arsenic (maximum)	.45
Sulfur (maximum)	.05
Iron (by analysis) (minimum)	14.00

This generally reflects the domestic industry's specification for standard high-carbon ferromanganese, usually considered as 74 to 76 percent manganese. Other important manganese ferroalloys, with their approximate manganese or other significant content ranges, are as follows: Low-carbon ferromanganese (80 to 95 percent Mn), medium carbon ferromanganese (80 to 85 percent Mn), silicomanganese (65 to 68 percent Mn, 12 to 20 percent Si), and spiegeleisen (up to 30 percent Mn, but usually between 16 and 23). Other intermediate and special manganese ferroalloys are marketed under various trade names. Briquets are ferromanganese or silicomanganese fines which have been bonded together so as to provide a standard known weight (for example, 2 pounds) of elemental manganese. They are used chiefly by iron foundries.

Several grades of electrolytic manganese metal are produced in the United States, including the regular, nitrided, hydrogen-removed, and hydrogen-reduced grades. National Stockpile Specification P–98–R2, Manganese Metal-Electrolytic, May 17, 1961, requires a minimum manganese content of 99.9 percent. Electric-furnace metal which had a minimum manganese content of 95.5 percent is no longer offered. Manganese metal, with a manganese content falling somewhere between these two, is produced abroad by the thermite process.

TECHNOLOGY

Geology

More than 100 minerals contain manganese as an essential element (*8*). Oxides, carbonates, and silicates, in that order, are the most important ore minerals or possible ore minerals of manganese. The principal manganiferous carbonate mineral is rhodochrosite, $MnCO_3$, which is one of an isomorphous series, including the carbonates of iron, calcium, magnesium, zinc, and cobalt, such that a great variety of intermediate compositions are to be found. The manganese oxide minerals frequently grade from one to another in composition with the result that identification is difficult and the terminology is confused. The common terms of 25 years ago, psilomelane, pyrolusite, and manganite, have been redefined by the mineralogist and are no longer acceptable to him in the manner in which they were formerly used. In recognizing the difficulties of applying to field use terms which have become narrow and dependent on X-ray or other laboratory examination, members of the Geological Survey have suggested "psilomelane type" in place of "psilomelane" to describe the hard massive oxides which are not specifically identified and which actually may be mixtures of more than one discrete oxide mineral. Similarly, the term "soft oxides" has been proposed for the soft black oxides which have not been specifically identified in the laboratory and which may be a mixture of several different manganese oxide minerals. In the same context, wad is an impure soft earthy mixture of oxides in which those of manganese predominate. Dana's System of Mineralogy,[3] however, applies the name,

[3] Dana, James Dwight, and Edward Salisbury Dana. The System of Mineralogy. John Wiley & Sons, Inc., New York, 7th ed., v. I, 1944, rev. by Charles Palache, Harry Berman, and Clifford Frondel, p. 566.

wad, "as a field or generic term to substances whose chief constitutent is a hydrous manganese oxide and whose true identity is unknown." It adds that these substances are largely mixtures. The difficulties with regard to the manganese oxides are compounded because fine-grained material may defy conclusive identification even with sophisticated laboratory equipment. Hausmannite, Mn_3O_4, and braunite, $(MnSi)_2O_3$, are distinct species which have been important as ores of manganese. Excluding braunite, the most important manganese silicate mineral is rhodonite, $MnSiO_3$, although it has not yet become an ore of manganese because of its refractory nature.

Geologically, manganese deposits are of a wide variety of types. The large and long-exploited Chiatura and Nikopol deposits of the U.S.S.R. are flat lying, or gently dipping, sedimentary deposits of relatively recent geologic age. On the other hand, metamorphic deposits of Madhya Pradesh, India, occur as tabular lenses conformable with the enclosing, intensely deformed and metamorphosed, ancient sediments. Examples of residual deposits are those of Madhya Pradesh associated with the metamorphosed deposits, the lateritic deposits of the Indian States of Orissa and Bihar (*7*), and the nodular ores in the residual clays of Arkansas and the southern Appalachians. The rhodochrosite ores of Butte and Philipsburg, Mont., are examples of manganese deposits occuring as steep-dipping hydrothermal veins and irregular replacement bodies.

One type of deposition may be superimposed on another, and the geologic history at a particular location may be quite complex. The highest grade ores are usually the result of oxidation and enrichment by circulating meteoric waters and the upper parts of many manganese deposits have experienced this activity to some degree.

In the United States the deposits of greatest interest as potential manganese resources are those of Aroostook County, Maine, the Cuyuana range, Minnesota, Chamberlain, S. Dak., Batesville, Ark., and Artillery Mountains, Ariz. All contain less than 10 percent manganese, except for the nodules at Chamberlain when they are considered by themselves.

The Aroostook deposits are more than 40 in number, scattered over an area some 70 miles long by 30 miles wide (*12*), grouped into northern, central, and southern districts. They are bedded in steep-dipping, folded and faulted, Paleozoic slates. The mineralogic character varies, but an extremely fine texture and intimate mixture of minerals are common to all. Iron content is roughly twice that of manganese. The largest known single deposit, Maple-Hovey Mountains in the central district, is complexly folded and faulted (*31*), and extends 1,500 feet below surface. The ore of this deposit is more siliceous than that of the other Aroostook deposits.

The low-grade Cuyuna range manganese deposits also extend to depth. They are of the following two classes: Unoxidized iron formation, commonly a manganiferous carbonate slate; and oxidized iron formation, either carbonate slate or chert, not sufficiently oxidized to be marketable as manganiferous iron ore or ferruginous manganese ore. They are of Precambrian age, are complexly folded, and have substantially higher iron than manganese content. Depth of oxidation extends to 500 feet or more. The presently merchantable manganiferous ores shipped from the range are the most highly oxidized material, and most of these ores now are concentrated before shipping (*25*).

Manganese occurs in a variety of associations in the Artillery Mountains region of western Arizona, but the occurrences of principal interest, because of large tonnages, are the extensive stratified deposits of manganese oxides in the Pliocene(?) sediments of the Chapin Wash formation. The manganiferous material has been classified as sandstone ore, clay ore, and hard ore. The latter is sandstone ore altered by weathering and circulating ground water. Perhaps two-thirds of the hard ore has been enriched in a few places to the extent that it averages more than 20 percent manganese. The upper manganiferous zone of the Chapin Wash formation outcrops along the Artillery Mountains as the northeast limb of a shallow syncline. Overlain by barren sediments and basalt, it extends continuously for 3 miles along the strike and is traced discontinuously for another 3 miles. Its thickness is variable, but is frequently on the order of 165 feet. Another manganiferous zone, from 750 to 1,000 feet stratigraphically lower, outcrops along the Rawhide Mountains on the southwest limb of the syncline. This lower zone consists of widely separated, relatively thin manganiferous lenses, and is up to 4 miles long by 350 feet thick (*23*). It does not have the promise of the upper zone and has not received as much investigation.

In south-central South Dakota, a horizontal deposit of manganiferous bentonitic shale, averaging roughly 40 to 50 feet thick in its central and northern portions, outcrops for many miles along both banks of the Missouri River and its tributaries. The deposit is particularly well exposed in the general vicinity of Chamberlain. Manganese-iron carbonate concretions, averaging 15.5 percent manganese and 9 percent iron, forming discontinuous layers 1 to 9 inches thick, constitute 3.8 percent of the principal manganiferous horizon. The manganese content of

this horizon otherwise has been indicated to be 1 percent (*32*). Associated with these deposits are smaller, but nevertheless extensive, deposits of gravels which carry a heterogeneous and irregularly distributed collection of manganiferous concretions having an oxide shell of varying thickness. A few of the concretions are completely, or almost completely, oxidized.

In the vicinity of Batesville, Ark., a large potential source of manganese remains as disseminated hausmannite, braunite, and rhodochrosite in the upper 15 to 50 feet of nearly horizontal, unweathered Paleozoic limestone, which outcrops along the hillsides (*36*). Most production of manganese ore from the district has been from deposits of manganese oxides occurring as lenses, pods, and disseminations in residual clays derived from weathering of the limestone. Although of relatively minor importance, some material from the residual deposits has been transported and redeposited as placers.

Mining

Manganese-mining operations range from primitive to those which are most modern and mechanized. The greater part of the world's manganese-ore production is from open pits or from underground mines using room-and-pillar or longwall systems of mining at relatively shallow depths. The recent trend has been toward open cuts, and greater mechanization.

Because of marked differences in the manner in which manganese deposits occur, a wide variety of mining methods are used—from square-set stoping in Montana to hydraulic underground mining in the U.S.S.R. Certain large low-grade U.S. deposits, because of their size and manner of occurrence, offer possibilities for development and use of exceptionally low-cost mining methods.

Just as there are no mining methods peculiar to manganese-ore mining—and for the same reasons of variable geological conditions and geographical habitat—neither are exploration, drilling and blasting, or loading and hauling operations distinctively identified with manganese ore mining. An exception is the now-completed mining operation of Manganese, Inc., at Henderson, Nev., where the necessity for uniform mill feed was met by using three blending and storage piles between mine and mill: One pile in process of accumulation, one in reserve as storage, and one in process of feeding the mill. The piles were built in 1-foot layers to heights of less than 20 feet, a record being kept of analysis of the ore as it was added to the pile. Stripping and mining operations, which included drilling, blasting, loading, and hauling, were under contract to a firm which specialized in western open-pit mining operations.

Mining of battery- and chemical-grade manganese ores must usually be selective, requiring experience on the part of the operator.

Manganiferous iron ores and ferruginous manganese ores for the most part are mined in the same manner as iron ores of the same district.

Beneficiation

Before 1950, few of the world's manganese ore producers had milling plants other than simple crushing, screening, and washing installations. Except for flotation and nodulizing of Montana carbonate ores, and magnetic concentration of Montana battery-grade ores, this was also largely true for the United States. With the high rate of industrial activity during and since the Korean war resulting in a heavy drain on the world's supply of high-grade manganese ores, more and more producers, both in foreign countries and in the United States, have installed heavy medium, jig, table, and other concentrating equipment, either alone or in various combinations. Sintering and nodulizing equipment also have come into greater use to agglomerate fines and to remove deleterious impurities, such as zinc and lead.

Beneficiation of manganese ores must not only increase the manganese content, but must also decrease the phosphorus below a prescribed maximum and obtain a proper manganese-to-iron ratio. Because of wide variation in the nature of manganese ores, there can be no standard treatment process.

However, the growth of custom mills in the United States was noted as the Government's domestic manganese purchase program progressed in the 1950's. Increasing centralization of milling in the U.S.S.R. was a feature of that same period and has been a feature of the following years, and it is believed that virtually all of the ores shipped now from both Chiatura and Nikopol undergo some concentration. Milling of the Chiatura ores of the U.S.S.R. involves crushing, washing on moving screens, jigging, and magnetic separation. Manganese recovery was reported to be 80 percent in the Chiatura plants in 1955, and it was expected that construction of a central plant for flotation of slimes, begun in 1956, would result in considerable reduction of the losses.

The two principal manganese-ore producers in the United States in the past decade, Manganese Inc., and The Anaconda Company, employed either oil-emulsion or conventional soap flotation as the major feature in beneficiating lowgrade ores—a wad ore of 10 to 20 percent

manganese content for the former, a carbonate ore of roughly 14 percent or less manganese content for the latter. By calcining the flotation concentrate in a rotary kiln Anaconda produced an oxide nodule containing approximately 57 to 58 percent manganese. Similarly, Manganese Inc. produced an oxide nodule containing 44 to 47 percent manganese, but at a high cost in reagents. In the Manganese Inc., operations reagent requirements per ton of ore varied from 120 to 180 pounds of lightweight petroleum oil, 25 to 40 pounds (dry weight) of soap, 5 to 10 pounds (dry weight) of a petroleum sulfonate, and about 8.5 pounds of sulfur dioxide (*18*). Economical treatment of this wad ore required that good manganese recoveries be made from slimes. Such recoveries were accomplished by intensive conditioning of the pulp by mechanical agitation after addition of all the reagents. This resulted in high power consumption.

Numerous hydrometallurgical processes reported in the Research section of this chapter have been developed for utilizing the manganese in the large low-grade domestic resources. Only one of these, the Dean-Læute ammonium carbamate process, has experienced successful commercial-scale operation. This was accomplished by producing synthetic manganese dioxide, a relatively high-priced item having a limited market. Using this process, roasted low-grade Cuyuna range materials were leached with ammoniacal ammonium carbamate solution to yield a high quality carbonate from which a wide variety of manganese end products were obtained. Careful control of the initial reduction step was necessary in order that the iron content be maintained in an insoluble form while the contained manganese was reduced to soluble manganous oxide. Control of temperature of the reacting slurry in the exothermic leaching step was also important to prevent loss of manganese carbonate in the slurry. Further, to achieve good recovery, care was required so that reoxidation of the manganous oxide did not occur (*39*).

Smelting and Electrometallurgy

The principal form in which manganese is used as such by the steel industry is as high-carbon ferromanganese, the greater part of which is made in blast furnaces and the remainder in electric furnaces. Virtually all spiegeleisen was made in blast furnaces until 1963 when one of the principal producers completed conversion to electric furnaces. Silicomanganese, medium carbon, low carbon, and special grades of ferromanganese are made in electric furnaces. Low-carbon ferromanganese is made commercially, also, by fused salt electrolysis.

The blast furnaces making ferromanganese or spiegeleisen are the same or similar to those making pig iron. It has been the case in a few plants, and may still be, that production of spiegeleisen or ferromanganese is obtained periodically from a pig-iron furnace by running it on alloy production long enough to build up a supply of alloy, after which the furnace is returned to its normal operation of producing pig iron.

Electric-arc furnaces used for making manganese ferroalloys are the same types as those used to make other ferroalloys, and there often is a certain amount of interchangeability in the scheduling of production of the various ferroalloys for any one furnace in a plant. Other materials such as calcium carbide, also, are made in the same types of furnace, but it is not good practice to use the identical furnace.

Both high-grade manganese ore and slag from electric furnace production of ferromanganese (*5*) are used as raw material for the production of electrolytic manganese metal. The Bureau pioneered in the production of electrolytic manganese from low-grade manganese ores, but commercial producers have found that costs favor the aforementioned materials. Regardless of the feed material used, a low iron content is desirable. Since 1957, a plant has been in operation in the Republic of South Africa producing electrolytic manganese from the manganese-bearing effluent of a mill leaching uranium ores.

High-, low-, and intermediate-grade manganese ores have each been used in the electrolytic production of synthetic manganese dioxide. As with the production of electrolytic manganese, costs are high. The best possibilities for producing a synthetic managanese dioxide more nearly competitive with natural dioxide ores appear to lie with chemical processes.

USES

The three major categories of use for manganese and manganese ore are metallurgical, dry-cell battery manufacture, and chemical including miscellaneous. Metallurgically, in the United States, manganese is used chiefly in the form of ferromanganese and to a lesser extent other manganese ferroalloys and manganese metal. For battery manufacture, either natural or synthetic battery-grade dioxide ore is used, although the large cost differential severely limits the quantity of synthetic dioxide consumed. In the chemical category a variety of manganese or manganiferous ores are employed, but the most important uses call for chemical-grade ore or its approximate equivalent.

The principal use of manganese is to counteract the harmful effects of sulfur in the production of steel. It is used for this purpose in the production of virtually all steels and consequently is essential to the quantity production of steel. The manganese addition acts as a deoxidizer as well, although it is not normally added for this purpose, a stronger deoxidizer such as ferrosilicon or aluminum being preferred (*1*). Silicomanganese is sometimes used as one alloy the manganese content of which counteracts sulfur, and the silicon content, with some help from the manganese, accomplishes the deoxidation. Manganese is used, also, as an alloying agent to impart one or more of the properties of strength, toughness, hardness, and hardenability to certain steels. The Hadfield or manganese steels, containing approximately 10 to 14 percent manganese and dating commercially from 1887 (*28*), are noted for the peculiar property of work-hardening, whereby hardness is increased by continued cold working under impact while the toughness and high ductility, which had been achieved by heat treatment, are retained. Manganese steel is limited in application to uses within relatively low-temperature ranges (*26*).

Other important metallurgical applications, although involving only small quantities, include the production of aluminum and magnesium. Manganese imparts strength, hardness, and stiffness to aluminum; hardness, stiffness, and corrosion-resistance to magnesium. A small manganese content in the magnesium bath inhibits alloying of magnesium with steel and so facilitates melting and alloying of the light metal in steel pots. Manganese additions to aluminum are made in the form of a master alloy containing 4 or 5 percent manganese, the balance being aluminum. Either electrolytic manganese or a special low-iron grade of ferromanganese is used in making up the master alloy. Manganese commonly is added to magnesium in the form of a flux, the major constituent of which is a manganese compound, usually manganese chloride. Manganese is alloyed with copper for the manufacture of manganese bronzes for ship propellers and other applications. High-damping manganese copper alloys have shown some promise, within limitations, for uses where vibration and noise are to be kept to a minimum. The principal use of manganese in the production of cast irons is to nullify the effects of sulfur.

Manganese ore, chiefly as the dioxide, has important uses in the chemical industry as an oxidizing agent in the manufacture of hydroquinone, and for the production of various manganese chemicals including potassium permanganate, manganese sulfate, manganous chloride, and manganous oxide. Hydroquinone is important as a photographic developer and has other uses; potassium permanganate is a powerful oxidant. A big use of manganese sulfate is as a fertilizer or fertilizer additive. It is important as a constituent of animal and poultry feeds and of fungicides, as a paint dryer, a coloring agent for the textile and ceramic industries, and as a base for the production of other manganese chemicals. Manganous chloride is used in dyeing textiles, in welding rod fluxes, and as a vehicle for alloying manganese with magnesium. Manganous oxide has a variety of uses, including fertilizer, animal and poultry feeds, and welding applications.

An important use of manganese dioxide, apparently poorly crystalline material, is as a depolarizing agent in the ordinary dry-cell battery. Hydrogen released from the electrolyte of the cell tends to form around the carbon electrode slowing down the action of the cell. This tendency is corrected by reaction of the hydrogen with available oxygen provided by manganese dioxide contained in the cell mix.

Other uses of manganese ore are in the production of synthetic manganese dioxide, in the leaching of uranium ores where it is used as an oxidant, in the manufacture of welding rods, welding rod coatings, ferrites, dyes, paint and varnish dryers, fertilizers, pharmaceuticals, frits, glass, and ceramics, and to give a variety of coloring effects to face brick. For certain of these uses, the ore is used directly; for others it may be processed first into compounds or salts of manganese. Manganese ore and manganiferous ores are used in base metal smelting and refining.

Where it is advantageous to introduce manganese in exceptionally pure form, such as in the production of stainless steels, certain chemicals, and the nonferrous metal industries, electrolytic manganese has become of increasing importance. Its use in the United States has grown from 2,000 short tons in 1954 to 19,000 tons in 1963.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

The demand for manganese depends upon the fortunes of the steel industry, varying in direct proportion to steel production.

The iron associated with many manganese ores is the most important coproduct of manganese. Although it is desired that the ratio of manganese to iron be kept at 6:1 or 8:1 in the production of ferromanganese, there is no restriction on the iron content of ores used in the production of pig iron. Because of the abundance of manganese and manganiferous ores in the U.S.S.R., they have been used much

more freely there in the production of pig iron than has been the case in the United States. Manganiferous iron ores and ferruginous manganese ores used in making pig iron are in effect essentially premium quality iron ores; their market and prices are tied to the iron ore market and price structure.

The lead, zinc, silver, or other nonferrous metal content of certain manganese ores contributes to the economics of their mining, and in certain instances means the difference between a successful operation and closed mine.

ALTERNATE MATERIALS

Although titanium, zirconium, and the rare-earth metals can assume some of the functions of manganese in steel, there are technical limitations to the extent to which they may be interchanged, as well as other problems of technology, cost, and supply. On the other hand, manganese has established itself as a replacement for part of the nickel of certain stainless steels, costs favoring the manganese.

A number of dry cells have been developed which do not use manganese, and their use is extending to more than the special applications, such as hearing aids, which had been their particular field.

The chemical and miscellaneous industries offer possibilities for use of other materials in place of manganese, and such substitutions are made when costs are favorable. Some of the best examples of this are the uses of manganese-dioxide ore as an oxidant, as in the processing of uranium ores.

SYNTHETICS

A synthetic manganese dioxide of high quality for use in dry cells is produced both electrolytically and chemically. High-grade, intermediate-grade, and low-grade ores are used as the raw material, but high costs of the processes limit use of the product. Where the ammonium carbamate process has been used as a preliminary step in producing synthetic managanese dioxide, high-purity manganese carbonate was obtained as an intermediate product. Some of this was sold as the carbonate, and some used to make other manganese chemicals in addition to its main use—that of producing the dioxide. In 1955, metallurgical nodules containing 60 percent manganese were the principal product made from it. In that it competed with natural ores, the chemically made manganese carbonate was considered a synthetic ore.

Certain processes developed for the utilization of manganese from low-grade or refractory ores have as their objective the production of high-manganese slag, or comparable material, which will be used in place of manganese ore as feed for the ferromanganese furnace. These materials might be considered synthetic metallurgical ores, and have been so termed (*3*), but none are being produced.

SECONDARY SOURCES AND RECOVERY

More manganese enters the steel-making process as a component of iron ores and of recycled open-hearth slags fed to the pig-iron blast furnaces, plus that in metal scrap fed to the open hearths, than is introduced via the medium of ferroalloys.

The quantity of manganese contained in the annual production of open-hearth slags has been approximately as much as that contained in the total manganese ore imported in some years. In 1952, it was estimated that 4.5 million tons of flush slags, averaging 9 percent manganese, and 7.25 million tons of tap slags, averaging 5 percent manganese, were being produced each year by integrated steel plants (*3*). Some of this slag, 25 percent or more, is recycled to the iron blast furnaces for its iron content and for fluxing effects—its manganese content serving only as a beneficial accessory. The possibility of using the wasted slags as a source of manganese for the production of ferromanganese has received much study (*4*). Because of mixing with other waste materials, accumulations of these slags on the dumps were believed to be too diluted and contaminated for serious consideration, but the daily outputs which would be contemporaneous with processing seemed to offer a good prospect. Slags from the basic oxygen furnace are sufficiently lower in manganese content than the open-hearth slags so that they do not appear interesting as an emergency source of manganese for the production of ferromanganese. In fact, their manganese and iron contents probably are not high enough to make them worth recycling to the blast furnace. With the expected rapid growth of the basic oxygen process of steel production supplanting the open hearth, the quantity of manganese available as a manganese source in open-hearth slags can be expected to decrease annually until these slags will no longer be worthy of further consideration for such recovery. Pig-iron blast furnace slags contain less manganese than do the basic oxygen process slags, and they have not been considered a possible source of manganese for the production of ferromanganese.

Electric-furnace ferromanganese slags are used in the production of other manganese

ferroalloys and electrolytic manganese. There may be some recycling of blast-furnace ferromanganese slags back to the blast furnace, but tonnages are not large and manganese contents are not high. The waste formed in pouring the metal from the furnace, which might run 20 percent manganese, is fed back to the furnace.

Some blast-furnace ferromanganese flue dusts are recovered, briquetted, clinkered, or sintered and fed back to the furnace. A high alkali content makes them otherwise undesirable.

In the chemical and uranium milling industries, where manganese dioxide is used as an oxidant, the spent liquors are a secondary source of manganese from which manganese sulfate and electrolytic manganese are obtained.

RESERVES AND RESOURCES

The United States has virtually no reserve of direct shipping manganese ore. Its reserves of ore from which a 35-plus percent manganese concentrate can be produced by normal concentration methods are scattered and may be given an order of magnitude of roughly 1 million tons, dependent to large extent on premium prices. There is a large low-grade domestic resource contained for the most part in the following five deposits: Aroostook County, Maine (*12*); Cuyuna range, Minnesota (*35*, *25*); Batesville, Ark. (*36*); Artillery Mountains, Ariz. (*23*); and Chamberlain, S. Dak. (*32*). The average grade of the manganese nodules occurring at Chamberlain is 15 percent manganese, but average for the deposit as it occurs in the ground is estimated at 1 to 2 percent. Manganese content of each of the other four deposits is less than 10 percent. Iron content of the deposits varies, being 33 percent for Cuyuna, 21 percent for Aroostook, 9 percent for the Chamberlain nodules, and less than 4 percent for both the Artillery Mountains and Batesville. Mining and metallurgical problems are inherent in recovering manganese from these low-grade natural resources, but for most of them research has indicated the problems to be surmountable at a cost—appearing better for some than for others.

The manganese reserve of the U.S.S.R. probably exceeds 1.5 billion tons containing from 16 to 49 percent manganese. More than 50 percent of this reserve is in the form of low-grade carbonate ores of which there has been little production as yet. Nearly one-third of the total reserve consists of metallurgical oxide ores of Chiatura and Nikopol, ranging from 25 to 49 percent in manganese content but apparently requiring concentration for the most part. Oxide and/or carbonate deposits are found in the Urals, both western and eastern Siberia, Kazakhstan, and the Far East. These ores are of low or intermediate grade but are being considered for exploitation in connection with regional development plans.

Manganese ore resources of mainland China have been estimated to total from 50 to 100 million tons of various grades, the better ores occurring south of the Yangtse River.

Gabon, Brazil, India, and the Republic of South Africa have a combined reserve of approximately 500 million tons of manganese oxide ore. In terms of ore in the ground, the basis apparently used in calculating the U.S.S.R. reserve, this is more than 800 million tons of oxide ore.

The Moanda deposits of Gabon have been estimated to contain approximately 200 million tons of merchantable ore with a manganese content of 48 percent, to be derived from 450 million tons of crude ore. This is as explored on three plateaus covering 35 to 40 square miles (*38*). Although most of the ore is metallurgical-grade material of excellent quality, a battery-grade ore containing 76 percent manganese dioxide is concentrated to obtain an 83 percent manganese dioxide product for use directly as a depolarizer in dry-cell batteries.

Recent estimates of Brazilian manganese ore reserves have been made which differ in providing totals on the order of 100 million (*33*) and 150 million tons (*16*). The latter figure contains a greater proportion in the inferred category not qualified as to grade. The largest reserve is in deposits in the Urucum district near the Bolivian border, estimated by Barbosa in 1956 to contain 70 million tons of ore (*8*). The later estimate of Abreu increased this to more than 100 million tons in including extension to the Serras Jacadiga and Mutum (*16*). Exploration to date of the Serra do Navio deposit of Amapa territory, northwest of the Amazon mouth, has established 30 million tons of ore of excellent quality, apparently with good possibilities for finding additional ore (*27*). The deposits of Minas Gerais, from which much of the past production has come, are estimated to have approximately 16 million tons (*16*), of which some 7 million tons contains more than 40 percent manganese and 8 million tons grades from 35 to 40 percent manganese (*8*). Bahia and Amazonas also possess reserves worthy of mention, and deposits are known in other States.

Manganese ores are widespread throughout peninsular India. Reserves of all grades in 1956 were estimated to exceed 100 million tons of mine-run ore, or the equivalent of 60 million tons of marketable ore. That of Madhya Pradesh alone was estimated in 1956 at 80 million tons of mine-run ore having a manganese content of approximately 35 percent. Other deposits of

importance are in northern Bombay State, Orissa, and Andhra (*8*). Allowing for production, 50 million tons of marketable ore is probably a likely current reserve figure for India.

No recent comprehensive estimate appears to have been made of the reserve of manganese ore in the Republic of South Africa other than recognition that it is extensive. The more enriched portions of the thick 50-foot (plus) lower ore body of the Kuruman field yielding ore in the 40 to 55 percent manganese range, suitably enriched to a width of 500 or 1,000 feet, is expected to provide many tens of millions of tons of ore when only 1 or 2 of some 20 miles of proven strike are considered.

If ore down to 30 percent manganese is included, a very large increase of reserve results for the thick lower body. In this grade range, it tends to a very attractive manganese to iron ratio of 7 to 1 or even 10 to 1. The upper 20-foot ore body, although thinner, appears to have a persistently higher metal content of 45 to 55 percent manganese, but its iron content is also high, being in the 5 to 15 percent range. Present knowledge concerning this upper ore body is scant, but it is indicated that a very large potential tonnage may be available (*2*). Kupferburger, in 1956, estimated conservatively for the Kuruman a probable ore reserve of well over 100 million tons of all grades down to 25 percent manganese content. At the same time, he estimated the potential reserve of the older Postmasburg field to be at least 20 million tons of ore ranging from 25 to more than 50 percent manganese (*8*). Production in the meantime has probably cut this down, with the result that a 12 to 15 million ton figure is ventured as probably being more indicative of the present status of Postmasburg reserves, assuming that the extracted reserves have not been replaced. On the other hand, the total manganese resource for the Kuruman conceivably can be double the 1956 reserve estimate of Kupferburger.

Manganese ore deposits occur in many other nations of the free world, but are small in comparison with those of the countries mentioned. In many instances they are not well defined as to quantity and/or grade.

Many locations on the deep ocean floors have a cover of manganese oxide nodules, which also contain nickel, cobalt, copper, and iron. Manganese dioxide analyses are quite variable and vary up to 63 percent (*9*). Estimates of total quantities of nodules involved in this potential resource have been in the billions, or even trillions, of tons.

CONSERVATION

In the steel-making process, manganese may be conserved to some extent by controlling slag volume through the use of molten pig iron low in silicon content, by making manganese additions to the ladle rather than to the furnace insofar as the quality requirements of the product will allow, by making silicon additions to the furnace before maganese additions, and by maintaining a high lime-slica ratio in the finishing slags. In 1949, a special committee of the American Iron and Steel Institute concluded that not more than 5 percent of manganese consumption could be saved by attention to such considerations in steel-making practices; and not more than 5 percent could be saved by changes in steel specifications, adding that perhaps another 5 percent or more might be saved by concerted action of the industry if processing difficulties of producers and consumers received secondary consideration. In the latter connection, the effects on surface quality, production rates, safety factors, and minimum job requirements must be taken into account (*1*).

The use of other alloys—silicomanganese, spiegeleisen, off-grade ferromanganese, silicospiegel—in place of ferromanganese offers some possibilities in savings of high-grade manganese ore in that low-grade or off-grade ores may be used for their production. The applications are limited, the possibilities of higher operating costs are to be considered, and conservation of manganese itself does not necessarily result. Silicomanganese is recognized to have certain advantages over ferromanganese in the production of deoxidized and partly deoxidized steels, particularly those of low-carbon content. Consumption of silicomanganese has increased to 16 percent that of ferromanganese from 8 percent in 1941.

SOURCES OF STATISTICAL INFORMATION

Statistics for domestic production and consumption of manganese ore, manganiferous ores, and manganese products, are obtained on a voluntary reporting basis by regular canvasses of the Bureau of Mines.

United States import and export statistics are collected by the Bureau of the Census from data obtained by the Bureau of Customs from the importer or exporter. Lack of incentive for the importer to report accurately information which is of no particular concern to the

Bureau of Customs apparently results in an appreciable number of errors of classification and also of country of origin. Where these are apparent and of some consequence, efforts are made to have the questionable data checked.

Statistics on foreign ore production, alloy production, ore and alloy consumption, and trade in both ore and alloy are compiled by the Bureau of Mines from annual questionnaires sent to consular offices, official statistical publications of foreign governments, State Department dispatches, and other sources. Difficulties in this area include confusion as to grade, units of nomenclature, and inadequate data. The different bases for reporting these data by the different countries may require considerable adjustment for their correct interpretation.

PRODUCTION, CONSUMPTION, AND TRADE

World production of manganese ore is shown in table 1. This table is based essentially on an arbitrary cut-off grade of approximately 30 percent manganese content, although production of some countries continues to be included even though grade has dropped below that point. Their ores are essentially the same as the ores of higher grade which were previously mined, and they are put to the same uses. The grades given in the percent manganese column of the table are not meant to be firm figures, but are only estimates to provide a comparative idea of grade. Because of the number of years covered by the table, and the frequent lack of definite information with regard to grade for a country's production in any one year, they can not be more than this. The figures followed by a plus mark are rough minimums with no limit set for the maximum.

The tonnages for the largest producer, the U.S.S.R., are not qualified as to grade, nor are they identified as shipping product, crude ore mined, or one of these converted to a pre-set grade base. There is good evidence, however, that the figures represent shipping product of which approximately 90 percent can be considered to be a good metallurgical ore, or its equivalent, and the remainder to be an intermediate grade ore.

U.S. record production of 366,000 short tons in 1957 was generated by the Government's domestic manganese purchase program, and production for other years has approached this only in 1918, 1956, and 1958. U.S. production dropped off rapidly upon termination of this program.

The United States and the U.S.S.R. are the largest consumers of manganese and of manganese ore, no other country being comparable to either in tonnage consumed. The large U.S. consumption coupled with its small production of ore makes this Nation the world's largest importer of manganese ore. Other ore-deficient consuming countries which are to be reckoned as importers of substantial quantities of ore are the United Kingdom, West Germany, France, the Benelux group, Japan, Norway, Italy, and Canada (*8*). All of these nations export ferromanganese to the United States, as do also Brazil, Chile, Mexico, Yugoslavia, India, Republic of South Africa, Spain, and Sweden. Some of these are ore-producing countries which have increased their capacity to produce ferromanganese with the intention of becoming, as much as possible, an exporter of alloy rather than ore.

Except for electrolytic manganese, exports are not an important part of U.S. foreign trade in manganese. Consumption of manganese ore in the United States is given in table 2; U.S. imports of manganese ore are given in table 3. Prior to 1949, the U.S.S.R. was an important supplier of manganese ore to the United States. These shipments were cut off by a Soviet embargo and have not been resumed, although Soviet manganese ore is again an important item in the world manganese trade. Barter deals of various kinds are also a factor in world trade of managanese ores and alloys.

U.S. tariffs on manganese ore, metal, and ferromanganese are set forth in table 4.

STRATEGIC CONSIDERATIONS

In 1958, U.S. production of manganese ore equaled 22 percent of the quantity consumed in the country, a higher ratio than the 15 percent or less which had normally prevailed since the Korean war. However, most of this 1958 production went to government stocks with the result that only 3 percent of the total manganese ore consumed actually was of domestic origin. Imports from Western Hemisphere sources equaled 63 percent of consumption in 1958, and a Western Hemisphere sufficiency of approximately 85 percent was attained.

In 1963, U.S. production of manganese ore was only a token quantity compared with consumption, and both imports from Western Hemisphere sources and Western Hemisphere sufficiency equaled 62 percent of consumption.

Government stockpile accumulations exceed the maximum objectives for metallurgical, battery, and chemical grades of manganese ore. Inventories on June 30, 1964, are shown in table 5. In addition stocks of ferromanganese, manganese metal, and non-stockpile-grade metallurgical ore have been acquired.

TABLE 1.—*World production of manganese ore by countries* [1] [2]

[Short tons]

Country [1]	Percent Mn [3]	1954–58 (average)	1959	1960	1961	1962	1963
North America:							
Costa Rica (exports)	35+						661
Cuba	36–50+	209,604	[4] 58,806	[5] 17,644	[3] [4] 46,000	[3] 83,000	[3] 83,400
Mexico [3]	44–46	190,800	181,900	171,400	155,900	184,900	189,300
Panama		[6] 3,321					
United States (shipments)	35+	306,352	229,119	80,021	46,088	24,758	10,622
Total [3]		710,077	469,905	269,100	248,000	292,700	284,000
South America:							
Argentina	30–40	19,174	21,358	24,251	[3] 22,000	11,253	[3] 11,000
Bolivia (exports)					53	291	
Brazil	38–50	548,081	1,138,649	1,101,387	1,120,336	1,290,461	[3] 1,320,000
British Guiana	40–42			123,811	216,203	303,636	157,331
Chile	40–50	48,646	42,744	50,594	35,012	47,578	51,235
Peru	40+	9,473	2,803	1,655	3,879	7,403	1,089
Venezuela	38+	[7] 17,429	3,955				
Total		642,803	1,209,509	1,301,698	1,397,483	1,660,622	[3] 1,540,700
Europe:							
Bulgaria	30+	62,189	28,700	27,600	40,800	38,600	42,400
Greece	35+	18,826	38,581	34,410	31,195	[3] 33,100	[3] 22,000
Hungary	30–	146,250	170,086	135,888	137,610	142,447	[3] 132,300
Italy	30–	53,969	57,520	54,561	54,196	49,053	49,920
Portugal	35+	6,009	7,703	8,197	12,492	12,666	[3] 20,500
Rumania	35	278,628	216,910	192,872	227,076	208,337	[3] 220,500
Spain	30+	41,975	44,924	24,586	17,092	14,101	16,631
U.S.S.R. [8]		5,463,900	6,080,300	6,472,800	6,583,000	7,057,000	[3] 7,385,000
Yugoslavia	30+	6,159	8,911	14,676	15,595	16,357	8,964
Total [1]		6,077,905	6,653,635	6,965,590	7,119,056	7,571,661	[3] 7,898,000
Asia:							
Burma	42+	1,539	606	324	196	213	[3] 220
China [3]	30+	556,000	1,100,000	1,320,000	880,000	880,000	1,100,000
Goa	32–50	147,498	83,584	118,195	109,790	96,732	[4] 115,290
India	35+	1,712,337	1,298,472	1,321,411	1,355,868	1,306,914	1,184,983
Indonesia	35–49	58,495	47,172	12,026	14,007	5,460	[3] 1,700
Iran [9]	30+	4,752	2,425	8,488	2,315	2,205	[3] 1,100
Japan	32–40	272,289	383,699	357,131	335,236	340,162	305,506
Korea, Republic of	30–48	2,312	496	1,521	1,518	1,105	[4] 580
Malaysia	30+			3,222	7,130	341	7,696
Pakistan	42+		32	327	386	15	
Philippines	35–51	17,253	38,365	19,159	20,986	13,160	6,769
Thailand	40+	[7] 645	452	582	588	3,194	7,186
Turkey	30–50	5,292	39,341	31,112	33,069	23,422	6,949
Total [3]		2,778,000	2,995,000	3,193,000	2,761,000	2,673,000	2,742,000
Africa:							
Angola	38–48	31,483	39,314	25,728	22,695	9,115	
Bechuanaland	30+	[6] 7,228	20,138	25,032	31,737	26,458	11,878
Congo (Léopoldville)	48+	414,771	425,694	420,671	350,208	329,568	348,547
Ethiopia	51		1,455	10,202	7,716	6,614	
Gabon, Republic of	50–52					224,038	701,716
Ghana (exports) [10]	48	622,902	577,694	600,261	431,282	513,622	434,410
Ivory Coast	38+			67,917	137,502	139,265	153,291
Morocco	35–50	470,829	518,711	532,508	629,512	517,377	369,283
Northern Rhodesia	30+	33,425	60,297	59,299	56,901	51,501	38,856
Southern Rhodesia	30+	1,292	2,126	1,676	205	7,977	
South Africa, Republic of	30+	784,525	1,069,202	1,316,132	1,562,729	1,614,599	1,441,503
South-West Africa	45+	65,184	49,442	67,439	50,295		
Sudan [3]	36–44	[7] 7,700	440				
United Arab Republic (Egypt) [11]	35+	15,504	67,318	22,046	2,272	42,577	53,628
Total		2,454,843	2,831,831	3,148,911	3,283,054	3,482,711	3,553,112
Oceania:							
Australia	45–48	60,827	100,768	67,923	97,901	77,851	[3] 40,500
Fiji	40+	23,001	14,566	13,073	3,869	1,202	3,621
New Hebrides	52–55				5,060	21,859	28,016
New Zealand	48+	155	114	134			
Papua	46	8		54	2		4
Total		83,991	115,448	81,184	106,832	100,912	[3] 72,100
World total (estimate) [1]		12,748,000	14,275,000	14,959,000	14,915,000	15,782,000	16,090,000

[1] Czechoslovakia and Sweden report production of manganese ore (approximately 13 to 17 percent manganese content), but since the manganese content averages substantially less than 30 percent, the output is not included in this table. Czechoslovakia averages annually 165,000 short tons and Sweden approximately 11,000 tons the last 5 years.

[2] This table incorporates some revisions. Data do not add exactly to totals shown because of rounding where estimated figures are included in the detail.

[3] Estimate.

[4] Exports.

[5] United States imports.

[6] Average annual production 1957–58.

[7] Average annual production 1956–58.

[8] Grade unstated. Source: The industry of the U.S.S.R., Central Statistical Administration (Moscow).

[9] Year ending March 20 of year following that stated.

[10] Dry weight.

[11] In addition to high-grade ore shown in the table, Egypt produced the following tonnages of less than 30 percent manganese content: 1954–58 (average), 154,816; 1959, 72,752; 1960, 282,191; 1961, 304,663; and 1962, 162,102.

TABLE 2.—*U.S. consumption of manganese ore (35 percent or more manganese content)*

Year	Manganese ore consumption (thousand short tons)				Steel production (ingots and steel for castings) (thousand short tons)	Manganese ore consumed per ton of steel produced (pounds)		Manganese content of ore imported for consumption (percent)	Manganese content of ore consumed [1] per ton of steel produced (pounds)	
	Total	By metallurgical industry	By chemical and miscellaneous industries	By battery manufacturers		Total all uses	Metallurgical use only		Total all uses	Metallurgical use only [2]
1954–58 (average)	1,995	1,928	36	31	103,707	38.45	37.18	45.97	17.68	17.09
1959	1,606	1,525	52	29	93,446	34.37	32.64	47.27	16.25	15.43
1960	1,946	1,853	66	27	99,282	39.20	37.33	47.54	18.64	17.75
1961	1,702	1,599	75	28	98,014	34.73	32.63	48.02	16.68	15.67
1962	1,865	1,753	78	34	98,328	37.93	35.66	47.73	18.10	17.02
1963	1,842	1,719	95	28	109,261	33.72	31.47	47.04	15.86	14.80

[1] Excludes manganese contained in iron ores, manganiferous ores (containing less than 35 percent Mn), or in secondary materials such as scrap or recycled slag. Assumes manganese content of ore consumed is approximately the same as that of ore imported for consumption.
[2] Includes manganese in form of ore (containing 35 percent or more Mn) used in making pig iron.

GOVERNMENT PROGRAMS

The defense program at the time of the Korean war and the following period, vigorously pursued with regard to manganese, took several forms: Stockpiling of ore and alloy, expansion of plant capacity, development of new plants using new processes, extensive research, and conservation through allocations. These ends were achieved by means of purchase contracts, advancement of funds or loans for exploration and development, accelerated tax amortization, research and development contracts, technical assistance for foreign lands, and incentive prices for home production. The results were reflected in record imports and record production.

The most noteworthy achievement of the program was the buildup of Government stocks of manganese ore by means of purchase contracts for widely scattered foreign ores. The large deposit of high-grade ore in Amapa, Brazil was brought into production in January 1957 as a result of an Export-Import Bank loan and a Defense Materials Procurement Agency purchase contract.

The domestic manganese purchase program, started in 1951, was essentially of two parts: The so-called "carlot" program calling for metallurgical ore to be purchased by the Government at railhead; and the depot program for low-grade ores to be purchased in quantities as small as 5 tons at depots established at Deming, N. Mex., Butte and Philipsburg, Mont., and Wenden, Ariz. The "carlot" program terminated August 5, 1959, and the last depot program was completed in May 1958.

The domestic exploration program of Defense Minerals Exploration Administration provided assistance for exploration for manganese on a participating basis to the extent of 75 percent of the approved exploration costs, the money to be repaid from proceeds of future production. A revised program has continued to offer assistance under the Office of Minerals Exploration with the Government's share of the costs cut to 50 percent, but there has been little activity as regards manganese.

Manganese ore, ferromanganese, and manganese metal enter prominently into contracts for barter of surplus U.S. agricultural products under the program conducted by the Office of Barter and Stockpiling, Foreign Agricultural Service, U.S. Department of Agriculture. In some contracts, the alloy and metal are produced in the United States from foreign ores imported especially for the purpose; in other contracts the ferromanganese may be produced abroad.

The supply requirements and stockpile position of manganese is reviewed at periodic intervals by the interested Government agencies, with consideration given to indicated actions such as acquisition, upgrading, and disposal.

PRICES

All manganese ore prices are by negotiation, being dependent on chemical analysis, physical structure, quantity offered, included freight and insurance costs, delivery terms, whether duty is included or excluded, needs of the buyer, and availability of ores of the desired quality. As a result, published quotations can only reflect the general condition of the market. Continuing quotations of the same basis, for metallurgical-grade ore, are of value in showing the price trend over a period.

The cost of ocean freight makes up approximately one-third the price of imported ore delivered at eastern seaboard ports. Consequently, an appreciable change in ore price can be entirely apart from any demand or supply factors. Prices for domestic ore in commercial markets are governed by the price of foreign ore and relative transportation costs. From 1951 to August 5, 1959, the Government price for domestic ore under the domestic purchase program re-

TABLE 3.—*U.S. imports of manganese ore (35 percent or more Mn), by countries*

Country	General imports [1]				Imports for consumption [2]					
	Short tons				Short tons				Value	
	Gross weight		Mn content		Gross weight		Mn content			
	1962	1963	1962	1963	1962	1963	1962	1963	1962	1963
North America:										
Guatemala	310		170		310		170		$15,516	
Mexico	133,629	147,607	59,876	66,930	135,828	145,390	60,899	65,922	3,897,010	$4,278,712
Total	133,939	147,607	60,046	66,930	136,138	145,390	61,069	65,922	3,912,526	4,278,712
South America:										
Brazil [3]	823,714	875,576	398,129	412,190	887,441	929,419	428,036	438,421	31,504,474	28,487,662
British Guiana [4]	145,188	105,655	61,087	45,141	43,490	115,216	18,805	51,019	945,390	2,530,948
Chile	4,970	1,784	2,203	749	4,970	1,784	2,203	749	127,935	32,005
Peru	6,070	4,025	2,553	1,767	1,461	8,400	643	3,593	37,501	139,766
Total	979,942	987,040	463,972	459,847	937,362	1,054,819	449,687	493,782	32,615,300	31,190,381
Europe:										
Greece	2,873	6,445	1,379	3,068	1,565	6,445	750	3,068	85,817	331,780
Sweden		92		46		92		46		4,182
Total	2,873	6,537	1,379	3,114	1,565	6,537	750	3,114	85,817	335,962
Asia:										
Goa [5]		2,369		1,096						
India	177,820	169,267	81,263	77,314	201,678	232,992	93,068	106,175	5,233,044	5,239,105
Philippines	7,459		3,402		7,459		3,402		169,138	
Turkey	6,970	4,443	3,298	2,087	6,942	7,596	3,300	3,532	227,030	207,699
Total	192,249	176,079	87,963	80,497	216,079	240,588	99,770	109,707	5,629,212	5,446,804
Africa:										
Angola [6]	1,378	45,752	758	22,118	21,627	52,813	10,861	25,703	610,551	1,393,418
British East Africa						345		195		15,302
Congo (Léopoldville), and Ruanda-Urundi	88,157	234,044	42,716	117,296	97,242	246,755	47,361	122,723	2,717,186	7,299,495
Ethiopia	6,936	3,854	3,468	1,978	6,936	3,854	3,468	1,978	255,581	147,063
Ghana	204,245	102,047	103,714	52,345	229,733	184,309	115,067	93,349	8,703,310	5,975,538
Morocco	125,003	38,221	66,275	20,097	121,974	40,906	64,670	21,621	6,496,493	1,943,327
Portuguese Western Africa, n.e.c.						7,913		3,739		216,564
Rhodesia and Nyasaland	10,800	3,550	5,405	1,792	12,558	3,550	6,277	1,792	400,970	126,986
South Africa, Republic of	195,804	120,568	81,496	50,406	169,560	239,064	71,998	99,284	3,901,037	5,026,432
United Arab Republic (Egypt)					13,160		6,380		555,111	
Western Africa, n.e.c. [7]	11,019	12,622	5,069	6,311		12,622		6,311		360,000
Western Equatorial Africa, n.e.c. [8]	17,807	215,552	8,727	108,253	38	150,055	20	74,889	1,770	3,649,534
Total	661,149	776,210	317,628	380,596	672,828	942,186	326,102	451,584	23,642,009	26,153,659
Oceania:										
Australia					3,986		2,012		174,528	
British Western Pacific Islands					1,591		764		29,741	
Total					5,577		2,776		204,269	
Grand total	1,970,152	2,093,473	930,988	990,984	1,969,549	2,389,520	940,154	1,124,109	66,089,133	67,405,518

[1] Comprises ore received in the United States; part went into consumption during the year, and the remainder entered bonded warehouses.
[2] Comprises ore received during the year for immediate consumption and material withdrawn from bonded warehouses.
[3] 1963 data adjusted by Bureau of Mines to include material reported by the Bureau of the Census from Uruguay.
[4] 1963 data adjusted by Bureau of Mines to include material reported by the Bureau of the Census from Trinidad and Tobago.
[5] Reported by the Bureau of the Census as Southern and Southeastern Asia, n.e.c. believed to be Goa by the Bureau of Mines.
[6] 1962 data adjusted by the Bureau of Mines to include material reported by the Bureau of the Census from Belgium-Luxembourg.
[7] Believed to be Ivory Coast.
[8] Believed to be Gabon.

Source: Bureau of the Census.

TABLE 4.—*U.S. tariffs for selected manganese items, as of Dec. 15, 1964*

Item	Rates of duty [1]	
	1	2
Manganese ore, including ferruginous manganese ore, and manganiferous iron ore, containing over 10 percent Mn.	Free [2]	1 cent per pound contained Mn.
Ferromanganese:		
Containing not over 1 percent carbon	0.6 cent per pound contained Mn plus 4.5 percent ad valorem.	1.875 cents per pound contained Mn plus 15 percent ad valorem.
Containing over 1 percent but not over 4 percent carbon.	0.9375 cent per pound contained Mn	1.875 cents per pound contained Mn.
Containing over 4 percent carbon	0.625 cent per pound contained Mn	1.875 cents per pound contained Mn.
Manganese metal	1.875 cents per pound plus 15 percent ad valorem.	1.875 cents per pound plus 15 percent ad valorem.

[1] Duty rate 1 is applicable for most nations; duty rate 2 is applicable for U.S.S.R., Mainland China, and certain other specified Communist countries.
[2] On June 30, 1964, the duty of 0.25 cent per pound of contained manganese was suspended for a period of 3 years.

mained constantly based at $2.30 per long-ton unit of manganese for manganese ore containing 48 percent manganese. This was usually about twice the market price, but had been as much as three times. A long-ton unit of manganese is 22.4 pounds of contained manganese.

Prices of the principal manganese items, reduced to comparable bases, are shown approximately for comparative purpose in table 6.

TABLE 5.—*Manganese materials in Government inventories*

[Thousand dry short tons]

Manganese	National strategic stockpile	DPA inventory	CCC stocks	Supplemental stockpile	Total
Battery-grade, natural	144			138	282
Battery-grade, synthetic dioxide	21	4			25
Chemical-grade, Type A	29			118	147
Chemical-grade, Type B	2			99	101
Metallurgical-grade	5,230	1,351	111	3,676	10,368

TABLE 6.—*Approximate comparative prices, November 1964*

Item	Per pound (gross weight)	Per short ton (gross weight)	Per pound of contained Mn
Manganese ore, metallurgical grade (48% Mn)	1.5¢	$30.00	3.1¢
High carbon ferromanganese (domestic, 74–76% Mn)	7.5	150.00	10.0
Medium carbon ferromanganese (80–85% Mn)	14.9	297.00	18.0
Low carbon ferromanganese (85–90% Mn, 0.10% max. C)	23.6	472.50	27.0
Silicomanganese (18–20% Si, 1.5% max. C)	8.3	166.00	12.5
Spiegeleisen (19–21% Mn)	3.9	77.68	19.4
Electrolytic manganese metal (regular grade)	30.0	600.00	30.0

TAXES

The U.S. depletion allowance is 23 percent for domestic manganese mining properties, 15 percent for foreign.

TRANSPORTATION

The large tonnages involved and the remote location of most manganese deposits makes transportation—both ocean and overland—a significant factor in development and exploitation.

The problems inherent in the long sea routes traversed, up to halfway round the world, are at times complicated by a shortage of vessels, port congestion, and by high ocean freight rates which constitute part of the price. These complications were very evident when the Suez Canal was closed.

The rail systems of a number of the large producing countries are not able to keep pace with the ability of the mines to produce, or with the demand for their ores. In addition, certain ores must be moved long distances before railhead or shipping port is reached. In Mexico this is a matter of 100 miles by truck over difficult terrain; at the Urucum deposits of Brazil, a river barge trip of some 1,200 miles is made before the ocean vessels are reached; and in Gabon an aerial tram line 45 miles long delivers the ore to the railroad.

In the United States, the cost of the long rail haul to the principal markets, which are in the East, decidedly limits the commercial potential of western ore sources, and limits the market for western ferromanganese.

RESEARCH

Intensive research on manganese by government and industry began around World War I. During each of the two World Wars as well as the Korean war and the immediately following years the Bureau of Mines and the Geological Survey investigated U.S. manganese supply potentialities. In the course of this work, virtually every known manganese occurrence was examined. The Bureau alone has made hundreds of examinations and investigations of domestic manganese deposits and of methods for utilizing them.

In 1935–36 the Bureau conducted pioneering research on the feasibility of producing electrolytic manganese from low-grade ores. Subsequent research by both industry and the Bureau led to commercial production of this metal beginning in 1939. An outgrowth of this work of the Bureau has been its development of high-damping manganese-copper alloys having high strength and unusually low thermal conductivity. Bureau research is credited with making possible the commercial production and acceptance of silicomanganese. Commercial application of soap flotation to western manganese ores and of the ammonium carbamate leach (Dean-Leute) process to Cuyuna range materials were also developments stemming from Bureau research.

The Bureau's ore dressing studies have contributed to successful operation of many of the Nation's small marginal deposits and could play an important part in helping the economics of the more complicated hydrometallurgical and pyrometallurgical processes which have been under consideration for utilizing the large low-grade and offgrade resources. The Bureau is currently engaged in evaluating these processes which have been under investigation by both the Bureau and industry.

One of the major Bureau investigations on manganese involved field work to explore and develop the "hard ore" in the Artillery Mountains deposit of Arizona, with detailed laboratory and pilot plant investigations of oil-emulsion flotation, dithionate leaching, sintering, and electric furnace smelting of concentrate to ferromanganese. Other fields of intensive endeavor have been the development of a selective reduction-oxidation process for obtaining a synthetic ore in the form of a high manganese slag from open-hearth slags, chloride volatilization of Maine manganiferous materials, differential sulfatization of manganiferous carbonate slate and other prospective ores from the Cuyuna range of Minnesota, a combination of the lime-clinkering (Sylvester) and ammonium carbonate leach processes as applied to open-hearth slags, the acid leaching of Aroostook and other manganiferous materials, the melt-quench-leach process for rhodonite and other siliceous feed materials, the acidulated ferrous sulfate or "pickle-liquor" leaching of offgrade manganiferous ores, and basic research on manganese and its compounds.

Industry, universities, and research institutes, independently and in cooperation with various agencies of the Government, have made important contributions to manganese research. For the most part these efforts have had a shorter range aspect than those of the Bureau—often tied to a particular process and/or a particular deposit. Basic research has been left largely to the Bureau of Mines.

Research by industry, either with or without Government assistance, has resulted in substantial interest in a number of processes for utilizing the Nation's large low-grade manganese resources. One of the more highly publicized processes has been that of Nossen Laboratories, Inc., constituting a cyclic nitric-acid leach in which manganese dioxide is produced after the manganese content of the feed has been reduced to manganous oxide. The Bruce Williams process (Ores Beneficiation Inc.) produces manganese carbonate after roasting a mixture of feed and ammonium salts. It is cyclic except for that part of the ammonia which is chemically destroyed. The Sylvester (Sylvester & Co.), or lime-clinkering, process is designed particularly for highly siliceous feed materials. Open-hearth slags or other low-grade siliceous manganiferous feeds are mixed with the proper proportions of limestone before roasting to a clinker, the magnetic fraction of which contains most of the manganese and iron. The Sheer-Korman high-intensity arc process, sponsored by Vitro Corporation of America, has as its particular objective the utilization of rhodonite deposits. A mixture of rhodonite and carbon is shaped into an electrode which is vaporized in a high-intensity arc. Manganese is then extracted from the resulting powder by leaching with sulfuric acid (*6*). The Udy electric furnace process of Strategic Materials Corp. employs specially designed electric furnaces in a two- or three-stage selective reduction smelting operation to produce high-, medium-, or low-carbon ferromanganese from siliceous ferruginous low-grade materials.

Among processes that received earlier attention, the sulfur dioxide leach of Manganese Ore Co. was tried on an operating scale during World War II. The many difficulties experienced in the operation of this plant, using Three Kids (Nevada) ore containing approximately 18 percent manganese, have been attributed in large part to the jump from a 1-ton-per-day pilot plant to an operating plant having a capacity of 1,000 tons per day, and to the wartime shortages of materials and trained personnel. The operation was not successful and was halted within a year of its start. The Bradley-Fitch ammonium sulfate process, previously tested on Cuyuna range material in a 4-ton-per-day pilot plant at the Minnesota School of Mines, was considered to be less desirable than leaching with sulfur dioxide gas. One of the reasons given was the greater wartime availability of sulfur as compared to ammonia.

Other processes, parts of processes, variations of above-mentioned processes, and combinations of parts of processes, have been proposed and studied in laboratory or pilot plant. A failing of many of these propositions is that too many steps are involved to allow much hope for favorable economics. Some of the products of these processes are in reality synthetic ores which must still compete with relatively low priced, good quality, imported ore.

Much research on different methods for producing high-quality synthetic manganese dioxide was conducted by industry under sponsorship of the U.S. Army Signal Corps for about 10 years. Previously, investigators at the National Bureau of Standards and elsewhere studied the constitution of manganese dioxide with particular regard to its suitability for battery manufacture. It was determined that there are several types of manganese dioxide. Although it is generally considered that the best material for batteries is a poorly crystallized form, and analysis and certain tests give indications of suitability, as yet no means have been found which will take the place of an actual use test to determine whether a particular natural or synthetic dioxide ore will be desirable for battery use.

OUTLOOK

The impact on manganese consumption of the anticipated steady growth of the basic oxygen process of steelmaking is difficult to assess for lack of conclusive information. Although the higher bath temperature of the basic oxygen furnace causes some manganese to revert from the slag to the metal, other factors may very well balance out the resulting drop in manganese requirements. For one, the iron and manganese contents of the slags resulting from the basic oxygen process probably will be too low to warrant their recycling to the blast furnace, as is done now with open hearth slags. This will result in a deficiency in manganese content of the hot metal charged to the steel furnace.

In view of the uncertainties involved in these and similar considerations, it is believed reasonable to project that manganese ore consumption will continue in approximate direct relation to the production of steel. An examination of table 2 shows the average of the last 5 years to be approximately 36 pounds of manganese ore consumed for all uses per short ton of steel produced. The fluctuations in the yearly rate suggest the futility of drawing conclusions too finely, and it is most probable that the net effect of the various factors involved will be less than these yearly variations. However, the possibility of a lower demand for manganese at some future date cannot be completely dismissed.

The world supply of good quality manganese ore is substantial, well distributed in a general way, and probably not a matter of concern for the next 25 years as long as the producing sources remain politically available to the consuming countries. The trend toward more beneficiation and other processing before export from the ore-producing countries may be expected to continue.

In the event that foreign supplies should no longer be available to the United States, this country will develop the more favorably situated—both technologically and geographically—of its low-grade natural domestic resources. As the basic oxygen process of steelmaking grows, steel furnace slags will become less and less attractive as a possible domestic manganese resource.

The outlook for battery-grade ore supply has improved with Gabon expected to take over the production of quality ore as the Ghana deposits become exhausted. No particular growth in consumption of these ores is foreseen because of the trend toward smaller batteries and the growing use of rechargeable batteries which do not contain manganese.

PROBLEMS

Efforts to make the United States self-sufficient with respect to manganese have been interrupted by withdrawal of the immediate need through the availability of abundant ores of high quality in other free world countries at favorable prices. The basic problem remains, however, with the following two differences: (1) One of the more favored sources, steel plant slags, has become less promising as a major domestic resource, and the load is correspondingly shifted to the natural deposits; and (2) the problem now appears essentially to be one of scaling up the most likely process for a particular resource to pilot plant or commercial operation. The problems of low manganese content, variations in chemical and physical nature in the same or different materials, intimately fine mixtures of manganese with other minerals, refractory nature of certain of the manganese minerals, manganese-to-iron and manganese-to-phosphorus ratio considerations, unfavorable locations, costs of mining, and recovery of by-products or coproducts, now are believed to be largely problems of economics for most of these materials. An exception to this statement is probably the Chamberlain deposit, the status of its technology appearing to be less satisfactory than that for the other four natural deposits.

Removal of the tariff on manganese ore for 3 years accentuates the problem of the domestic battery ore miner to mine, mill, and market an acceptable product at a price which can compete with imported ore.

The overriding problem of the potential western metallurgical manganese ore or alloy producer, apart from the availability of good foreign ore, remains one of transportation to markets. The problems for the eastern alloy producer are those of foreign alloy imports, overcapacity with an appreciable part in the form of outmoded plant or equipment, and low-profit margins. The potential eastern ore producer has the problem of ore imports, coupled with virtual exhaustion of good ores in the eastern part of the country.

There is no satisfactory substitute for manganese in its major metallurgical uses, and manganese as a metal has no uses of its own. Knowledge concerning the properties of the pure metal is limited and confused by incon-

sistencies and contradictions in the published data.

Continued adequate supply of foreign manganese ores is subject to the hazards and delays inherent in transportation over long sea and rail routes and to unfavorable actions on the part of the producing countries, such as imposition of embargoes, export taxes, royalties, port and other charges, and any actions arising from the compelling wish to do as much processing within the country as is economically possible. The demands of other manganese consuming countries are to be reckoned with as well.

When considering these factors, the problems of stockpiling become more pointed: How much? In what form? Where? Under how much surveillance? What are to be the conditions for disposal?

The production and export of manganese is an important factor in the economies of most of the major ore-producing countries, and the United States is an important market. These countries are faced with a problem of oversupply in the world market.

Discussions of supply and requirements still have the problem of the degree of interchangeability among the different grades of ore, and the problem of inadequacy of foreign supply statistics on a grade basis and of foreign consumption or stocks data on any basis.

While the deposits of the ocean floors are believed to represent very large manganese resources, the problems connected with their eventual exploitation are many. These include the depths at which they occur, actual physical recovery of the ore from the bottom, storage and transportation to land, metallurgical separation and recovery of the valuable constituents, and the problems of ownership and international law.

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MERCURY

By John E. Shelton [1]

THE PRINCIPAL commercial mineral of mercury is the red sulfide, cinnabar, which usually occurs in small irregular deposits at comparatively shallow depths. Although cinnabar occurrences are known throughout the world, those of economic importance are limited to a few areas.

Mercury production is relatively small and in quantity ranks 10th in world output of nonferrous metals. Italy and Spain dominated world mercury production and furnished almost half of the 236,000 flasks produced in 1963. Other countries producing smaller but significant quantities included China, Japan, Mexico, the Philippines, the United States, the U.S.S.R., and Yugoslavia. Of the 19,000 flasks of mercury produced in the United States in 1963, California supplied 71 percent; Nevada 26 percent; and Alaska, Arizona, Idaho, and Oregon the remainder. Arkansas, Texas, Utah, and Washington have produced mercury in the past.

Consumption of 78,000 flasks in the United States in 1963 was the highest in history. It resulted from the large requirements for expansion and installation of plants to produce chlorine and caustic soda. Large quantities were also used for replacement of losses in the electrolytic preparation of chlorine and caustic soda, in electrical apparatus, in industrial and control instruments, and in chemicals for agriculture and industrial purposes. Appreciable but smaller quantities were used in precision castings, dental preparations, general laboratory applications, and mildew-proofing paints.

For many of mercury's uses, satisfactory substitutes are known or could be developed; however, there are few satisfactory substitutes for uses that depend upon mercury's liquidity at ordinary temperatures, high specific gravity, and electrical conductivity. Consequently, large-scale substitution is deterred except when shortages of mercury are severe and continued.

The United States is not self-sufficient in mercury and depends on imports, mostly from Italy, Mexico, Spain, and Yugoslavia, for part of the supply.

To bolster domestic production, to provide stability to the industry, and to assure an adequate supply of mercury, the Government has a program providing exploration assistance.

Production and consumption of mercury should continue to rise both in the United States and in foreign countries. However, until production rises or other sources of supply become available, the price of mercury is expected to rise.

The domestic mercury industry is confronted with several problems, principally the necessity of finding additional ore reserves, impediments to efficient and low-cost procedures for recovering mercury, and the lack of a stable market.

BACKGROUND

SIZE AND ORGANIZATION OF THE INDUSTRY

World production of mercury is relatively small and ranks 10th in quantity of output among the nonferrous metals. In the United States production of mercury at individual mines ranges from a few to about 8,000 flasks, and usage at individual consumers ranges from a few pounds to about 10,000 flasks per year.

Only one of the domestic mercury producers—the Buckman Laboratories, Inc.—is considered a vertically integrated company. The other producers sell virgin mercury through brokers and dealers or directly to consumers. Some consumers act also as brokers and dealers.

Foreign mercury operations differ from those in the United States principally in the number, size, and ownership of mines. In most instances only one or two mines furnish virtually the entire output of a foreign country; in addition, the mines in Italy, Spain, and Yugoslavia are wholly or partly State owned and controlled.

[1] Commodity specialist.

Mercurio Europeo, a cartel of Spanish and Italian producers, was formed in 1928 when world stocks of mercury were excessive. The aims of the organization were distribution of sales, control of production, and stabilization of prices. Spanish and Italian producers controlled over 80 percent of world production at the time; sales were allocated 55 percent to Spain and 45 percent to Italy. The cartel was formally disbanded January 1, 1950, after the U.S. Government purchased a large quantity of Italian mercury with counterpart funds.

In January 1958 it was announced that mercury production of the Monte Amiata and Siele operations in Italy would be marketed by a joint sales office, Mercurio Italiano. Mercurio Italiano was dissolved on January 1, 1963, because of antimonopoly rules of the European Common Market. The two companies were to operate separately thereafter.

GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Mercury occurrences are known in many countries; however, only a few produce mercury, and Italy and Spain dominate world production. Virtually all the Spanish production comes from one large mine, the Almadén, Province of Ciudad Real; Italian production comes from two large mines in the Monte Amiata area. Other major producers are China, Mexico, Japan, the United States, the U.S.S.R., Yugoslavia, and the Philippines.

The principal mercury-producing States are California and Nevada, with smaller quantities produced in Alaska, Arizona, Arkansas, Idaho, Oregon, Texas, Utah, and Washington.

In 1963, 8 mines furnished 97 percent of domestic primary production, about 40 other operations supplying the remainder.

State and county:	*Mine*
Alaska: Aniak District	Red Devil.
Arizona: Maricopa	National.
California:	
San Benito	New Idria.
San Luis Obispo	Buena Vista.
Santa Clara	New Almaden.
Sonoma	Culver-Baer.
Nevada:	
Humboldt	Cordero.
Nye	Ione.

Of the 300 companies which consume virgin mercury, 80 account for about 96 percent of the total domestic consumption and are mainly in the Eastern United States. About 400 companies throughout the United States use approximately 20 percent of the total annual consumption in redistilled form.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Mercury produced by the mines is known as prime virgin mercury and usually contains more than 99.9 percent mercury. Virgin metal with a clean and bright appearance contains less than 1 part per million of any base metal and is satisfactory for nearly all uses. There are no overall market specifications, but market quotations cover only virgin mercury in flasks of 76 pounds.

Flasks for prime virgin metal are made of wrought iron and spun steel. There are many variations in diameter, height, and weight, ranging as follows: Diameter, 4 to 7 inches (usually in the upper part of this range); average height, about 12 inches; weight, 7 to 15 pounds, averaging about 8 pounds.

Reclaimed mercury, generally as clean as the virgin metal, may contain more gold and silver when not subjected to distillation in the reclaiming process.

Grades of mercury other than virgin are produced by concerns that reduce the impurities in virgin metal by multiple distillation or other means.

General Services Administration Material Purchase Specifications P–31–R1, dated May 27, 1958, for purchases for the national stockpile require prime virgin mercury that averages not less than 99.9 percent mercury and that "shall be bright and clean."

TECHNOLOGY

Geology

The principal ore mineral of mercury is the red sulfide, cinnabar (HgS—86.2 percent mercury and 13.8 percent sulfur). The native metal occurs in some ores; mercury has also been obtained from livingstonite, metacinnabarite, and approximately 25 other minerals. Pyrite and marcasite and small quantities of other sulfides, such as arsenic and antimony, often are associated with the cinnabar.

Mercury deposits usually occur at relatively shallow depths, and almost entirely in regions of volcanic activity. The ore bodies are not true veins and were deposited in irregular chambered veins and brecciated zones, as stockworks of minute seams, and as disseminations and replacements in porous rock. The common gangue rocks are limestone, calcareous shales, sandstone, serpentine, chert, andesite, basalt, and rhyolite.

Cinnabar ore may be classified into two general types—disseminated ore, in which the cinnabar has impregnated a fine-grained or highly

brecciated gangue, and ores deposited in fissures and cracks of the country rock. The second type of ore merges into the first as the fissures and cracks become very minute. At the other extreme are veins and bodies of almost pure cinnabar sharply separated from the gangue. The porosity of the rock determines the grade of the ore formed; open-textured sandstone or coarse breccia yield generous space for deposition of high-grade ore bodies, whereas receptacle rocks such as shales or schists give little room for deposition. Proper trap structures, such as clay gangue or relatively impervious rock, are necessary for localizing the ore-bearing solutions in the receptacle rock.

Mining

Mercury ore is mined by both underground and surface methods. Of the two types, underground mining furnishes approximately 90 percent of the mercury production in the United States.

At the larger underground mercury mines, square-set stoping or some modification is most frequently used, although sometimes shrinkage and sublevel stopes are employed. After the ore has been broken by conventional drilling and blasting, it is removed by scrapers, by direct drop to drawpoints, or by mechanical loaders. Hand tramming is used, for short distances, but locomotives are used for longer hauls. The ore is either trammed or hoisted to the surface.

Open pit or surface mining is done by the usual drilling, blasting, and loading. Power shovels or mechanical loaders, usually of less than 1-cubic-yard capacity, are used to load gasoline- or diesel-powered dump trucks that haul the ore to the extraction plant.

Operations in the United States mine as much as 300 tons of ore per day at underground mines and 175 tons per day at open pits. Underground mines average less than 5 tons per man-shift, but open pit production per man-shift ranges up to 40 tons. Consequently, at the lower cost open pit mines, ore that averages as low as 3 pounds of mercury per ton is mined, compared with about 8 pounds per ton at underground mines.

Metallurgy

Milling of mercury ore consists of crushing, sometimes followed by screening. The principal purpose of these operations is to reduce the material to a size required for furnacing; mercury minerals crushing easier and finer than the gangue rock can be upgraded by screening and rejecting the larger pieces of low-grade or barren material. The material also can be upgraded by hand sorting. Gravity concentration by jigs and tables has been attempted but with little success due to excessive losses in slimes. Concentration of mercury minerals by flotation is efficient and produces a high-grade concentrate. Despite the necessity of fine grinding and an ample water supply, the treatment of low-grade ores by flotation before roasting or leaching is advantageous.

Mercury is extracted from ore and concentrate by heating in retorts or furnaces to liberate the metal as a vapor, followed by cooling of the vapor and collection of the condensed mercury. Retorts are inexpensive installations for small operations and require only simple firing and condensing equipment. They are best adapted to operations treating 500 pounds to 5 tons per day of high-grade sorted ore. One of the most objectionable and costly features of retorts is the manual charging and removal of material.

For larger operations, either rotary or multiple-hearth furnaces with mechanical feeding and discharging devices are preferred. It is unnecessary to size the feed, which may range up to 3 inches for rotary and 1.25 inches for multiple-hearth furnaces. Standard furnace capacities range from 10 to 100 tons per day with larger sizes to suit requirements. Mercury-laden gases pass from the furnaces through dust collectors into the condensers, where the vapor is cooled and the mercury is collected. Final traces of mercury in the gases from the condensers are removed in washers, and the stripped gases are discharged through a stack into the atmosphere. The mercury from the condenser always contains some dirt and soot, which are separated by hoeing the mixture with lime. Mercury from this operation is clean and sufficiently pure for marketing.

Mercury also can be leached from its ores and concentrates with a solution of sodium sulfide and sodium hydroxide and recovered as the metal by precipitation with aluminum or by electrolysis (*22*).[2] Leaching of mercury ores has not been practiced extensively because of reagent-consuming constituents in some ores, irregularity in compositions of ores, and the cost of fine grinding. However, recent studies have indicated that some of these objections can be overcome by concentrating the ore by flotation and leaching the resulting concentrate.

Mercury Poisoning

Poisoning may occur in mining and extracting metallic mercury and in any industry in which mercury is used, as a result of handling or exposure to its vapor. The Bureau of Mines and many other organizations have studied the subject and issued reports.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

Precautions that should be taken to insure the safe mining and handling of mercury include proper ventilation of working areas, use of respirators or gas masks, personal cleanliness, spraying contaminated surfaces with various compounds to render the mercury inert, use of mercury vapor detectors, and periodic physical and dental examinations.

USES

One of the large and growing uses of mercury is as a cathode in the electrolytic preparation of chlorine and caustic soda. Actual consumption of mercury in this manufacturing process is small for each unit, although large quantities are required for the original installation. Because of the large number of plants now in operation, the requirement for mercury to replace losses has become a major use.

Large quantities of mercury are also used in electrical apparatus and in industrial and control instruments. Applications include the use of mercury in various lamps, arc rectifiers, batteries, switches, thermometers, barometers, and related equipment. Significant quantities of mercury are used in dental preparations, as catalysts, and in general laboratory applications; small quantities are consumed in amalgamation and manufacturing fulminate for detonators.

A relatively new application of mercury is in frozen mercury patterns for precision casting. Owing to its smooth surface and low uniform expansion upon heating, mercury is superior to wax or plastic pattern materials.

Compounds of mercury are used extensively in insecticides, fungicides, and bactericides for agricultural and industrial purposes. Pharmaceuticals, the control of slime in pulp and paper mills, and protective paints use smaller but appreciable quantities of mercury compounds.

Uses that may become important are catalysts in manufacturing organic compounds, pigments, and new applications of amalgam metallurgy. The latter use will depend upon results of current and future research studies.

ALTERNATE MATERIALS

Other processes are available to replace those using mercury as a cathode in the electrolytic preparation of chlorine and caustic soda and in boilers for generating power. For agricultural and industrial purposes, copper and numerous organic chemicals may be substituted for mercury compounds. In the pharmaceutical field, sulfa drugs, iodine, and various antiseptics and disinfectants may be used instead of mercury chemicals. In some dental uses, metal powders, porcelain, and plastic materials are preferred to mercury amalgams. Lead azide, diazodinitrophenol, and other organic initiators may replace mercury fulminate.

There are few satisfactory substitutes for those applications in electrical apparatus and industrial and control instruments that depend on mercury's high specific gravity, fluidity at normal temperature, or electrical conductivity.

SECONDARY MERCURY

Secondary mercury furnishes a significant part of domestic supply. Production in 1963 was 10,520 flasks. Of the total, approximately 4,000 flasks of excess Government mercury was transferred to other Government agencies. The balance, about 6,500 flasks recovered from dental amalgam, oxide and acetate sludges, and battery scrap, represented 25 percent of the total domestic production of primary and secondary mercury. Virtually all metal can be reclaimed from mercury cells, mercury boilers, electrical apparatus, and control instruments, when the plant or equipment is dismantled or scrapped.

RESERVES

The Bureau of Mines studied the potential resources of mercury at 1,000 domestic mines, prospects, and occurrences thought capable of contributing to future production. Table 1 shows the reserve potential at these 1,000 properties at selected price levels, based on 1961 costs and technology.

TABLE 1.—*Mercury resources of the United States at selected price levels*

[Thousand flasks [1]]

State	Mercury price per flask					
	$100	$200	$300	$500	$1,000	$1,500
Alaska		14.5	33.5	69.5	124.5	142.5
Arizona			2.5	8.0	12.0	13.5
Arkansas				4.5	6.5	7.5
California	39.0	112.5	258.0	566.5	853.0	941.0
Idaho			20.5	37.5	65.0	72.0
Nevada	7.5	13.0	34.5	71.5	115.5	157.5
Oregon			12.5	34.5	55.0	71.0
Texas			17.5	35.0	54.0	59.0
Utah					.5	.5
Washington				.5	1.0	1.0
Total	46.5	140.0	379.0	827.5	1,287.0	1,465.5

[1] Flask as used in this chapter refers to a 76-pound flask.

Resources of 140,000 flasks at $200 per flask represent ore grades of about 10 pounds of mercury per ton at most domestic mines and about 20 pounds of mercury per ton of ore in

the very narrow veins in Alaska. A country-wide average of 5 pounds of mercury per ton of ore is equivalent to a total resource of about 575,000 flasks at $400 per flask, based on costs in 1962.

World reserves of mercury minable under economic conditions existing in 1957 and 1962 were estimated by the Federal Geological Survey. In 1957–62 the reserves of mercury in the United States decreased about 80,000 flasks owing to depletion of ore by mining the known reserves and lack of exploration because of declining prices. Almost all of the measured and indicated reserves were in mines active at the end of 1961. World reserves in thousand flasks are shown in table 2.

TABLE 2.—*World reserves of mercury*

[Thousand flasks]

Country	1957		1962	
	Measured and indicated	Inferred	Measured and indicated	Inferred
Canada	150	150		
China		500		400
Czechoslovakia	10		5	
Italy	500	1,000	200	500
Japan	30	50	30	30
Mexico	30	100	25	100
Philippines	45	45	35	
South America	4	10	10	10
Spain	100	1,000	500	500
Turkey		50		40
United States	125	190	45	30
U.S.S.R.	850	500	150	150
Yugoslavia	150	300	100	300
Total	2,000	3,900	1,100	2,100

The data for Spain are inadequate and the reserves may be much larger. The reserves of the U.S.S.R. may be larger considering the amount of exploration to the time of the estimate.

SOURCES OF STATISTICAL INFORMATION

Monthly and annual data on production, shipments, and stocks of mercury are obtained from domestic producers by the Bureau of Mines. Quarterly data on consumption, by end uses, are obtained from consumers and account for about 95 percent of the total consumed; users of small quantities of virgin mercury report annually; thus, 100-percent coverage is obtained. Some consumers who are also processors report quarterly the quantity of virgin mercury redistilled, and an annual survey is conducted to obtain the end use in which the redistilled mercury was consumed. Consumers also report stocks of mercury at plants and in transit. Brokers, dealers, and importers furnish quarterly reports showing receipts of mercury from abroad, purchases of domestic mercury, and stocks in bonded or free warehouses. A preliminary survey of dealers each year obtains data from small-quantity producers. The domestic data collected are sufficiently adequate and accurate for current programing and planning.

World production and trade data of foreign mercury-producing countries are also compiled by the Bureau. U.S. imports and exports of mercury are obtained by the Bureau of the Census, U.S. Department of Commerce. Mercury statistics on production for some foreign areas are not adequate.

PRODUCTION, CONSUMPTION, AND TRADE

Production

Italy is the leading mercury-producing country, followed closely by Spain. World production for 1963 declined 4 percent from a near-record high in 1962, primarily owing to the 7,177 flask decrease in U.S. output (table 3).

In 1963, California was again the leading producing State and Nevada remained in second place. Small quantities were produced in Alaska, Arizona, Idaho, and Oregon (table 4).

TABLE 3.—*Mercury produced in the world, by principal countries*

[Flasks]

Country	1954–58 (average)	1959	1960	1961	1962	1963
China [1]	14,500	23,000	23,000	26,000	26,000	26,000
Italy	58,503	45,833	55,492	55,434	54,535	54,564
Japan	4,997	5,988	5,791	5,437	4,409	[1] 4,500
Mexico	21,558	16,420	20,114	18,101	18,855	[1] 17,800
Peru	591	2,526	3,034	3,001	3,483	[1] [2] 2,600
Philippines	2,584	3,539	3,041	3,167	2,767	2,649
Spain	47,553	51,680	53,369	51,202	52,798	[1] 53,000
Turkey	905	1,479	1,339	1,864	2,687	[1] 3,000
U.S.S.R. [1]	19,300	25,000	25,000	25,000	35,000	35,000
United States	26,873	31,256	33,223	31,662	26,277	19,100
Yugoslavia	13,373	13,344	14,069	15,954	16,273	15,838
Other countries [3]	2,300	3,000	4,500	3,200	1,900	2,000
Total	213,000	223,000	242,000	240,000	245,000	236,000

[1] Estimate.
[2] Includes Austria, Chile, Colombia, Czechoslovakia, Rumania, and Tunisia.
[3] Exports.

Consumption

Annual consumption rose steadily from 51,200 flasks in 1960 to a record 78,000 flasks in 1963. Increases in the use of mercury were recorded in most major categories. The high rate of increased usage was due mainly to the large quantities used in the expansion and installation of new chlorine and caustic soda plants. The quantity involved in this use is shown under "Other" to conceal company confidential information (table 5). The consump-

tion of mercury also increased significantly in making electrical apparatus, in replacing losses in the manufacturing of chlorine and caustic soda, for mildew-proofing paints, and in pharmaceuticals.

The major sources of mercury imported into the United States are Italy, Mexico, Spain, and Yugoslavia. Small quantities are also imported from other countries (table 6). Some of these countries are normally importers of mercury, some of which probably is reexported to the United States.

A duty of 25 cents per pound ($19 per flask) on imports of mercury has been in effect since 1922.

TABLE 4.—*Mercury produced in the United States, by States*

[Flasks]

State	1954–58 (average)	1959	1960	1961	1962	1963
Alaska	2,642	3,743	4,459	4,129	3,719	400
California	13,806	17,100	18,764	18,688	15,951	13,592
Idaho	1,999	1,961	1,538	1,073	----	(1)
Nevada	6,046	7,156	7,821	7,486	6,573	4,944
Other States [2]	2,380	1,296	641	286	34	164
Total	26,873	31,256	33,223	31,662	26,277	19,100

[1] Included with "Other States."
[2] Includes Arizona, Oregon, Texas, and Washington, and data indicated by footnote 1.

TABLE 5.—*Mercury consumed in the United States, by uses*

[Flasks]

Use	1954–58 (average)	1959	1960	1961	1962	1963
Agriculture (includes fungicides, and bactericides for industrial purposes)	7,517	3,202	2,974	2,557	4,266	2,538
Amalgamation	230	265	255	278	299	306
Catalysts	774	965	1,018	707	874	612
Dental preparations [1]	1,405	1,828	1,783	2,154	2,033	2,346
Electrical apparatus [1]	9,670	8,905	9,268	10,255	11,564	11,115
Electrolytic preparation of chlorine and caustic soda	3,434	5,828	6,211	6,056	7,314	7,999
General laboratory use	990	1,110	1,302	1,484	1,752	2,085
Industrial and control instruments [1]	5,802	6,164	6,525	5,627	5,186	4,943
Paint:						
Antifouling	613	993	1,360	915	124	252
Mildew proofing	(2)	2,521	2,861	5,146	4,554	6,403
Paper and pulp manufacture	(3)	4,360	3,481	3,094	2,600	2,831
Pharmaceuticals	1,641	1,717	1,729	2,515	3,378	4,081
Redistilled [1]	9,500	9,331	9,678	9,013	8,987	9,227
Other	10,350	7,706	2,722	5,962	12,370	23,225
Total	51,926	54,895	51,167	55,763	65,301	77,963

[1] A breakdown of the "redistilled" classification showed ranges of 45 to 38 percent for instruments, 14 to 8 percent for dental preparations, 44 to 28 percent for electrical apparatus, and 18 to 8 percent for miscellaneous uses in 1954–62, compared with 44 percent for instruments, 13 percent for dental preparations, 25 percent for electrical apparatus, and 18 percent for miscellaneous uses in 1963.
[2] Data not available.
[3] Included with agriculture.

TABLE 6.—*Mercury imported (general imports) into the United States*

[Flasks]

Country	1954–58 (average)	1959	1960	1961	1962	1963
Canada	85	125	20	24	61	150
Chile	257	400	139	82	200	740
Italy	10,050	6,175	3,447	2,002	10,498	8,474
Mexico	9,305	3,631	2,459	3,205	7,560	4,328
Peru	211	599	49	----	----	3,406
Philippines	220	400	----	----	----	1,580
Spain	19,625	17,509	12,444	6,544	9,826	19,950
United Kingdom	613	185	----	(1)	(1)	----
Yugoslavia	2,525	954	910	355	3,301	4,498
Other countries	48	282	47	315	70	----
Total	42,939	30,260	19,515	12,527	31,516	43,126

[1] Less than 1 flask.

Source: Bureau of the Census, U.S. Department of Commerce.

STRATEGIC CONSIDERATIONS

From the beginning of mercury production in the United States in 1850 until 1918, output was ample to fill demands. Since 1918, however, except for 1931 and 1940 through 1942, it has been necessary to import mercury to satisfy industrial requirements. In 1950, domestic production was the lowest ever recorded and supplied only 9 percent of the requirements. Total production in the United States increased gradually and in 1958 supplied 83 percent of the domestic consumption; it then decreased to 38 percent of requirements in 1963.

During a war, the United States could probably attain self-sufficiency in mercury (table 7). Yet, at the 1963 rate of consumption, which probably would be exceeded during a war, mercury reserves would be adequate for only 2 years.

TABLE 7.—*U.S. self-sufficiency in mercury*

Year	Consumption (flasks)	Production		
		Mine (flasks)	Secondary (flasks)	Percent of consumption
1954	42,796	18,543	6,100	58
1955	57,185	18,955	10,030	51
1956	54,143	24,177	5,850	55
1957	52,889	34,625	5,800	76
1958	52,617	38,067	5,400	83
1959	54,895	31,256	4,950	66
1960	51,167	33,223	5,350	75
1961	55,763	31,662	8,360	72
1962	65,301	26,277	5,800	49
1963	77,963	19,100	10,520	38

As the availability of European mercury, which furnishes the major part of the U.S. imports has been restricted, if not eliminated, in wartime, mercury has been designated a strategic and critical material for stockpiling. The stockpile objective for conventional war was set at 200,000 flasks as of July 1963. On June 30, 1964, Government inventories totaled 200,501 flasks, of which 184,501 was in the national (strategic) stockpile, and 16,000 in the supplemental stockpile.

GOVERNMENT PROGRAMS

The Office of Minerals Exploration (OME) is authorized to grant loans up to 50 percent of the approved costs on exploration projects for mercury. From January 1, 1959 to December 31, 1963, OME executed eight contracts for exploration totaling $580,590.

In 1958, the U.S. Department of Agriculture announced that mercury was included in the list of material eligible for the supplemental stockpile through barter or exchange transactions, as provided by section 303 of the amended Agricultural Trade Development and Assistance Act of 1954. A total of 16,000 flasks was received from Spain under the program. Mercury was removed from the barter list in 1959, reinstated in 1961, and then removed in 1962.

The U.S. Tariff Commission held a public hearing on February 20, 1962, following its investigation of the mercury industry in 1961. Members of the mercury mining, selling, and consuming industries were present. The Commission report of November 1958 was updated and results were published in "Report to the Congress on Investigations No. 332–32 (Supplemental)," TC 57, May 1962.

In 1963, the Atomic Energy Commission reported that it held 50,000 flasks of excess mercury. Approximately 46,000 flasks was transferred to the national stockpile. The balance was transferred to various Federal agencies to meet their requirements.

PRICES AND COSTS

Average quoted prices of mercury at New York and London, 1954–63, are given in table 8.

Very little information is available on costs of production either in the United States or abroad; however, for comparative purposes it is noteworthy that Spanish ore averages about 50 pounds of mercury per ton; Italian, about 15 pounds, and United States, about 8 pounds.

TAXES

No special taxes are imposed on the mercury industry. Producers are granted a depletion allowance, 23 percent on domestic production and 15 percent on foreign production.

TABLE 8.—*Average yearly prices per flask of mercury at New York and London*

Year	New York [1]	London [2]	Year	New York [1]	London [2]
1954	$264.39	$255.33	1959	$227.48	$208.61
1955	290.35	280.22	1960	210.76	197.86
1956	259.92	238.68	1961	197.61	181.87
1957	246.98	232.36	1962	191.21	172.79
1958	229.06	214.98	1963	189.45	171.42

[1] Engineering and Mining Journal.
[2] Mining Journal (London).

RESEARCH

Investigations of the geology and resources of mercury are being made by the Government; mercury products research is undertaken almost exclusively by private industry.

The Bureau of Mines is evaluating the mercury resources of the Kuskokwim River Basin in Alaska. A study of the resource potential

in the United States is nearing completion. The Federal Geological Survey is studying the geology of selected mercury deposits.

Concentration of mercury minerals by flotation and optimum conditions for leaching and precipitation of mercury were investigated by the Bureau.

The Bureau's metallurgy research program investigated the recovery of waste metals by amalgam electrolysis. The studies were successful in recovering zinc from sal skimmings, ashes, and dross and in recovering tin from hardhead. Mercury was used to leach zinc and tin from the waste material to form amalgams of each metal, which were subsequently refined electrolytically to produce high-purity metal. Investigations are being made on refining commercially available metals to a superpure state by amalgam electrolysis. Some impurities in cadmium, indium, lead, tin, and high-grade zinc may be reduced from parts per million to a few parts per billion.

Most of industry's research is directed to developing new and improved mercury chemicals for agricultural, industrial, and pharmaceutical purposes and to improvements in utilization of mercury cells for producing chlorine and caustic soda. One new development is a mercury flywheel for stabilizing space vehicles in flight.

OUTLOOK

The demand for mercury is expected to rise throughout the world for the next 5 to 10 years. Plans in Asia, Europe, and North America to increase the production of chlorine and caustic soda, the principal use of mercury in recent years, indicate that requirements for mercury for this use will become greater. Technologic advancements resulting in a greater usage of mercury in mildew-proofing paints and the plastics industry, as well as increased use of mercury in dental and health applications and batteries, also will contribute to the rising demand.

Potential new uses of mercury may be in amalgam metallurgy and in ion exchange engines for deep space exploration. Availability and technical advancement will be important factors in how much mercury is used for these purposes.

World production will increase for the next few years. However, the increase in output probably will be about equal to the increased demand. Many mines in the United States have closed owing to depletion of reserves, decreasing grade of ore, and the downward trend in prices from 1957 to late 1963. Under the impetus of rising prices since 1963, exploration and development activities have increased, but it will be some time before domestic ouptut will rise significantly. The high-grade reserves of some of the large foreign producers are being depleted, but increased efficiency of operations and opening of new areas should result in increasing production. Although Italy and Spain should continue to be the major producers of mercury, other countries probably will produce a greater share of the total.

Demand for mercury in the United States will far exceed production; however, domestic production, releases of excess mercury by the Government, and imports should be sufficient to meet requirements.

Research by Government and industry is expected to continue. Improvements in ground support techniques, control of ground movement, and slope stabilization could lower mining costs and improve efficiency of recovery.

The quantity of mercury reclaimed from secondary sources has shown little change, except when a mercury boiler was removed from service or excess mercury held by the Atomic Energy Commission was made available. However, increased use of mercury in manufacturing processes and in batteries may result in expansion of the secondary industry.

PROBLEMS

The major problems of the U.S. mercury industry are the domination of the world market by a few relatively large low-cost foreign operations and the instability of the price of mercury. Domestic mines can produce mercury profitably and in large quantities only during periods of rising demand accompanied by firm high prices.

The narrow, irregular, and small size of ore deposits make impractical the use of large-scale development, mining, and metallurgical techniques to enable low-cost efficient mining and processing. Costly recycling or specific treatment of soot, dust, and residues is necessary to minimize the loss of mercury. High fuel and labor costs in many of the isolated areas makes the treatment of low-grade ores uneconomical.

Another problem is the gradual depletion of ore grade and reserves in currently producing mines. The depletion of ore reserves is due to curtailment of exploration while prices were decreasing from 1957 to late 1963 and is compounded because the narrow, irregular mercury occurrences make reliable estimates difficult. Deposits often may be bypassed during prospecting or exploration because overlying caps of rocks prevent detection.

The principal problem of the reclamation of mercury from secondary sources is that most scrap mercury-bearing items contain small quantities of mercury. The large ratio of extraneous materials raises recovery costs.

The toxic nature of mercury is an ever-present problem in the handling and treatment of mercury ores, especially when fumes and dust are present.

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MICA

By Benjamin Petkof [1]

THIN mica sheet, used in ancient Rome for windows, provides man with a natural material suitable for electrical and thermal insulation. Finely ground mica is used in many products ranging from paints to well drilling mud. The most important commercial varieties of mica are muscovite and phlogopite. This chapter is concerned principally with muscovite and to a minor extent with phlogopite, which is not produced commercially in the United States.

Because the domestic sheet mica industry produces only a small fraction of U.S. requirements for high-quality sheet mica, the electrical and electronic industries must import most of their sheet mica.

Muscovite sheet mica is recovered only from pegmatite deposits; phlogopite sheet mica is recovered from pyroxenites. Skilled hand labor is required to prepare sheet mica in forms suitable for stamping and punching into shapes and sizes required by the end user. Fabricating plants are situated principally in electrical-products manufacturing centers in the Eastern United States.

Scrap mica is mined from pegmatite deposits as a sole product; it also is a byproduct of mining, trimming, and fabricating sheet mica, or it may be recovered from disseminated deposits. Most scrap mica is ground, but increasing quantities are specially delaminated and reconstituted into sheets.

Sheet mica is an important dielectric and insulating material in the electronic and electrical industries. Ground mica is used as a filler and surface coating in numerous products, including roofing materials, wallboard cements, paints, rubber, plastics, and drilling muds.

Miniaturization of electronic components and development of some substitutes have reduced the total quantity of block and film mica required. Reconstituted mica is satisfactory for most applications now using built-up mica made from muscovite splittings and for some applications using built-up mica made from phlogopite splittings.

Synthetic mica is produced commercially by the internal electric-resistance heating process. Nearly all the product is a flake material which is ground for use in glass-bonded mica. Because large crystals are difficult to produce and recover, synthetic mica is not yet a substitute for strategic natural mica.

The measured reserve of sheet mica in the United States is insignificant, but resources of scrap mica are adequate.

The United States is not self-sufficient in any category of sheet mica or in high-quality scrap mica. Research has been focused on substitutes for strategic mica. Much of this has been government-sponsored research on synthetic mica, but some has been conducted by industry on synthetic mica, reconstituted mica, and other substitutes.

The long-range problem concerning sheet mica is the assurance of an adequate economic supply of the strategic categories of block and film or of a satisfactory substitute material. Research is needed to improve the competitive position of ground mica through better processing methods and to develop new uses for scrap and ground mica, particularly the lower qualities.

A comprehensive report on mica was published by the Bureau of Mines as one of its Materials Survey series on strategic mineral commodities (*26*).[2]

BACKGROUND

In ancient times mica was used for decorative and medicinal purposes and as a translucent or transparent sheet material. Later it became widely used in store windows, lamp chimneys, and lampshades. Because of heat resistance and transparency, only clear sheets were suitable for these applications. With the intro-

[1] Commodity specialist.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

duction of electrical appliances in the late 19th century, the consumption of sheet mica in the electrical industry soon greatly exceeded that for all other uses. In the electronic industry, mica became the preferred material as the dielectric material in capacitors and for electronic tube spacers.

Commercial production of mica in the United States began in 1803 at the Ruggles mine, Grafton County, N.H., and until 1868 New Hampshire furnished all the domestic mica. When mica mining began on a large scale in North Carolina soon after 1868, mica output from New Hampshire declined (*20*).

Production of sheet mica in the United States fluctuated greatly before World War II. Total output from 1880 to 1919, was 23,600,000 pounds. From 1920 to 1940, uncut sheet mica output ranged from 340,000 to 2,200,000 pounds per year. From 1940 to 1945, wartime demand and Government assistance through the Colonial Mica Corp. stimulated increased output. During this period, peak annual output was 3.5 million pounds in 1943, and the average annual output was about 2.3 million pounds. When the Government support program ceased in 1945, production declined sharply to 270,000 pounds in 1948. Under the Defense Production Act of 1950, as amended, the Government in 1952 instituted a domestic mica purchasing program which terminated in June 1962. From 1952 though 1963 the maximum annual domestic output of sheet mica was 890,000 pounds in 1956; of this total, 236,000 pounds was the calculated quantities of full-trimmed mica, equivalent to Government purchases under this program. In 1958 the corresponding figure for domestic mica sold to the Government was 274,000 pounds, the highest to date, while total sales of domestic sheet mica dropped to 660,000 pounds. This mica, valued at $2.8 million, was produced at about 600 operations, mostly small scale, with the 10 largest producers accounting for about 40 percent of the output.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Mica can be divided into two main classifications, sheet mica and scrap mica (including flake mica). Separate divisions of the mica industry produce these two classes of mica, which differ widely in their uses and in the forms in which they are marketed.

In addition to production by organized enterprises, substantial quantities of mica have been mined in off-seasons by persons with other primary occupations, particularly farming. Small, part-time mining operations supply a significant quantity of the total output of sheet mica.

Removal of adhering rock, dirt, and defective mica from the mine-run mica takes place either at the working face or at the surface of the mine. The resultant product, called handcobbed mica, is processed into sheet mica in small shops at the mine or shops accessible to a group of mines. The trimmed mica from these shops is shipped to a fabricator.

The fabricator stamps or punches trimmed sheet mica into specified shapes and sizes, in accordance with specifications of the ultimate consumer. The fabricating industry is highly specialized, and includes firms that fabricate the mica to supply the electronic and electrical industries and firms that manufacture electronic and electrical equipment and fabricate mica for their own consumption. In the United States in 1963, block and film mica was fabricated by 20 companies, and mica splittings were manufactured into built-up mica by 12 companies.

Increasing quantities of fully manufactured mica parts stamped to the exact dimensions and designs required for tube spacers, capacitor films, and various other uses also are imported into the United States from a number of countries. In some instances these fabricating operations in foreign countries are under the direction and control of manufacturers in the United States.

Scrap mica usually has been the dominant product of the U.S. mica industry, and in recent years more than 99 percent of the total tonnage of domestically produced mica has been scrap mica. In 1963 sales of scrap mica totaled 109,000 short tons, a record figure, and had a value of slightly less than $2.8 million. There were 29 producers of scrap mica during 1963, with 31 operations. North Carolina was the largest producing State.

Although mica is produced in a number of countries, the foreign sources of principal importance to the United States are India, Brazil, the Malagasy Republic, and Canada. Malagasy and Canada produce principally phlogopite mica. The others produce muscovite mica, the preponderant commercial variety.

Mica mining in the United States is confined largely to pegmatites in a few well-defined areas. The largest region extends from central Virginia southward through western North and South Carolina, northern Georgia, and east-central Alabama. A second region lies discontinuously in the New England States—New Hampshire, Connecticut, and Maine each possess mica-bearing pegmatites. A third region comprises districts in the Black Hills of South Dakota and in Colorado, Idaho, and New Mexico.

Although production of mica has been reported in 25 States, the outputs from only a few have been large. Throughout the years, North Carolina and New Hampshire have been the principal producers of sheet mica. The most important area has been the Spruce Pine, N.C., district in Avery, Mitchell, and Yancey Counties.

In 1963, North Carolina produced the bulk of the total output of domestic sheet mica and over half the tonnage of domestic scrap mica. Georgia, Alabama, and South Carolina furnished substantial quantities of scrap mica.

The fabricators of block, film, and splittings are situated principally in electrical products manufacturing centers, which lie outside the productive mica regions. However, several fabricators are in the North Carolina mica district. In 1963, fabrication of muscovite block and film mica was reported in 10 States, mostly near the east coast. About 51 percent (2.3 million pounds) of the total was reported by 12 companies in 3 States—New Jersey (5), New York (3), and North Carolina (4). Fabrication of splittings was reported in 9 States by 11 companies with 12 plants.

Reconstituted mica, often called mica paper, was produced in 1963 at Schenectady, N.Y., and Rutland, Vt.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Mica is a group name for a number of complex hydrous potassium aluminum silicate minerals differing in chemical composition and physical properties but characterized by excellent basal cleavage that facilitates splitting into thin, tough, flexible, elastic sheets. These minerals can be classified into four principal types, named after the most common mineral in each group, muscovite, phlogopite, biotite, and lepidolite. Muscovite (potassium mica) and phlogopite (magnesium mica) are the most important commercially and are the ones discussed in this chapter.

Muscovite mica is classified according to color. The Geological Survey has arranged mica into seven main color categories and three commercial groups (*14*). However, the National Bureau of Standards has established two color categories, ruby and nonruby, the color classifications used by the Government in purchasing mica for the stockpile.

The crystals of crude mica obtained from the mine in various shapes and sizes are called *books* because of the appearance given by the laminar structure.

Hand-cobbed or *cobbed mica* is the usable rough sheet mica that remains after all adhering rock, dirt, and defective mica has been removed from the books.

Rifting is the process of splitting the hand-cobbed mica into usable thicknesses.

Trimming removes broken and ragged edges, loose scales, and major imperfections. *Thumb-trimmed mica* is rifted mica from which the ragged edges have been removed with the thumb and fingers. *Half-trimmed mica*, which must have no cracks extending into the area by which the piece is graded, is rifted mica trimmed by cutting the ragged edges from two sides—the two adjacent sides of at least two-thirds of the pieces and the two parallel long sides of the balance of the pieces. *Full-trimmed mica* is rifted mica with the ragged edges cut from all sides in such a way that all cracks and corrugations are removed.

Sheet mica is relatively flat and sufficiently free from structural defects to enable it to be punched or stamped into specified shapes for use by the electronic and electrical industries. Sheet mica is classified further as *block*, *film*, or *splittings*, based on thickness. *Block mica* is not less than 0.007 inch thick with a minimum usable area of 1 square inch. *Film mica* is split from the better qualities of block mica to specified thickness groups ranging from 0.0012 to 0.004 inch. *Splittings* are sheets with a maximum thickness of 0.0012 inch, and a minimum usable area of 0.75 square inch. Small-sized, low-quality block mica is subdivided as *punch*, *circle*, and *washer mica*. *Punch mica* now includes all three and designates a thumb-trimmed material up to about 2 inches in diameter (*26*).

Block mica, based on the relative quantity of visible inclusions and structural imperfections in accordance with American Society for Testing and Materials (ASTM) specifications, is classed into 12 quality groups (described in table 1). Film mica is classified by ASTM as first, second, or third quality. First quality is equivalent to fair stained block mica, second quality to good stained block, and third quality to stained block. Using ASTM specifications based on the maximum usable rectangle, block and film mica can be classed into 12 size groups, or grades, ranging from the smallest, No. 6, to the largest, OOEE special. The sizes designated by these grades are indicated in table 2. Mica splittings are supplied in three commercial forms and in eight grades.

Strategic muscovite block and film mica is ruby and nonruby block, good stained or better qualities (the top four qualities), grade No. 6 or larger; ruby stained A/B quality (minimum 30 percent of fifth quality, maximum 70 percent of sixth quality), grade No. 6 or larger; and ruby and nonruby film, first and second qualities, grade No. 4 and smaller. Both muscovite and phlogopite splittings in certain cate-

TABLE 1.—*Visual classification of muscovite block mica*

ASTM visual quality	Commercial designation	Description [1]
V-1	Clear	Hard, of uniform color, nearly flat, free from all stains, foreign inclusions, cracks, and other similar defects.
V-2	Clear and Slightly Stained	Hard, of uniform color, nearly flat and may contain slight crystallographic discoloration, and very slight air inclusions in not more than one-fourth of the usable area.
V-3	Fair Stained	Hard, of uniform color, may contain slight waves, slight crystallographic discoloration, and slight air inclusions in not more than one-half of the usable area.
V-4	Good Stained	Hard, of uniform color, may contain medium waves, slight crystallographic discoloration, and medium air inclusions in not more than two-thirds of the usable area.
V-5	Stained A	Hard, may contain medium air inclusions uniformly distributed in the usable area, slight green vegetable stains, and medium waves.
V-6	Stained B	Hard, may contain heavy air inclusions and heavy waves, medium green vegetable stains, slight light black and red dots (mineral), and slight clay stains.
V-7	Heavy Stained	Same as V-6 plus medium cloudy stains and medium clay stains. Soft, buckles, ridges, and sand blast acceptable if specified.
V-7A	Densely Stained	Hard and soft. May contain heavy waves and air inclusions, heavy cloudy stains, heavy light black and red dots (mineral), medium black and red stains (mineral), medium buckles and ridges. Also green stains (vegetable type), clay stains, herringbone, and sand blast.
V-8	Black Dotted	Hard, may contain medium waves, heavy air inclusions, cloudy stains, light black and red dots (mineral), and green stains (vegetable).
V-9	Black Spotted	Same as V-8 plus slight black stains (mineral), and sand blast.
V-10	Black Stained	Same as V-8 plus sand blast, medium black stains (mineral), slight red stains (mineral), and clay stains.
V-10A	Densely Black and Red Stained.	Same as V-8 plus red stains (mineral), black and red stains (mineral), sand blast, slight clay stains, heavy black stains (mineral), and heavy waves. Soft acceptable if specified.

[1] From ASTM Specifications D351-60T.

TABLE 2.—*ASTM grades (sizes) of muscovite block and film mica*

ASTM grade	Area of minimum rectangle (square inches)	Minimum dimension of a side (inches)
OOEE Special	100	4
OEE Special	80	4
EE Special	60	4
E Special	48	4
A-1 (Special)	36	3½
1	24	3
2	15	2
3	10	2
4	6	1½
5	3	1
5½	2¼	⅞
6	1	¾

gories are classed as strategic materials, but none of the categories of phlogopite block and film is strategic (*2–3*).

National Stockpile Specifications P–32a–R1, Mica-Muscovite Block, Stained A/B and Better; P–32b–R, Mica-Muscovite Film; P–33–R, Mica-Muscovite Splittings; and P–34–R, Mica-Phlogopite Splittings, cover the physical requirements for the categories of mica designated as strategic or critical.

Built-up mica is a composite material built to any desired thickness by alternating layers of partly overlapped splittings and a suitable binder, usually organic. The mica is then formed into sheets, plates, or special configurations by heating, pressing, and trimming.

Reconstituted mica (mica paper) is a paper-like material consisting of fine flakes of scrap mica deposited as a continuous mat. The sheet usually is impregnated with an organic material.

Scrap mica, in the broad sense, is mica that because of size, color, or quality is below specifications for sheet mica. Scrap mica may be obtained from pegmatite deposits as a sole product or as a byproduct (mine scrap); derived from rifting and trimming sheet mica (shop scrap) and from fabrication waste (factory scrap); or recovered from schists and from the beneficiation of feldspar and kaolin (flake mica).

Synthetic mica, as referred to in this chapter, is produced by crystallization during the slow cooling of a melt of accurately proportioned raw materials. Although hundreds of micas can be synthesized by this process, normal fluorphlogopite mica is the composition that has been most promising for producing crystals having desirable mechanical and dielectric properties. In this composition, the hydroxyl ions of natural phlogopite are replaced by fluoride ions. In general, synthetic micas are true micas that have been manufactured by reacting suitable raw materials under proper conditions and need not be limited to fluorine micas.

TECHNOLOGY

Geology

Muscovite sheet mica is recovered only from pegmatite deposits. Zoned pegmatites are the principal source. Concentrations or shoots of mica are distributed sporadically throughout the deposit as books or crystals of various sizes and thicknesses. These crystals, usually roughly hexagonal and tabular, range from less than an inch to several feet in maximum dimension. It is not possible to identify reliably a potentially productive pegmatite dike or to establish the exact location of mica within a productive dike except by close sampling.

Large crystals of phlogopite usually are found in pyroxenite dikes in association with calcite and apatite.

Throughout the world the occurrence of higher quality and larger grades of sheet mica is irregular and spotty. Even in the famous Bihar mica field of India, only two or three veins in a hundred are said to be rich enough to permit development on an extensive scale. In all areas, low- and high-quality mica are found together.

Mica occurs widely as flakes in many igneous, metamorphic, and sedimentary rocks. The muscovite content of some schists and kaolins is high enough to be recovered for use as scrap mica.

Prospecting, Exploration, and Mining

The only practical method of prospecting for sheet mica is to sink test pits in the pegmatite to determine the percentage, size, and quality of trimmed sheet that might be obtained from a deposit. Preliminary stripping and trenching, usually by bulldozer or other mechanical equipment, may be used to outline the size, shape, and attitude of the pegmatite vein, either to aid in selecting the sites for test pits or to supplement the information obtained from the test pits. The most common method of exploration for sheet mica is to sink a shaft either down dip in the pegmatite body or vertically to cut the pegmatite at the desired depth. Drifts are then driven along the strike in both directions. Some pegmatites are explored by adits. Diamond drilling seldom is used to explore pegmatites for mica.

Most sheet mica mines are operated on a small scale. Open pit mining is economically feasible in relatively flat or gently rolling country where pegmatites occur at or near the surface and dip gently. Many mica-bearing pegmatite dikes are mined by underground methods. Care must be taken to avoid drilling through good crystals of mica. A low velocity, 40-percent dynamite usually is used in blasting around a pocket of mica, and only a few holes are blasted at a time to avoid shattering the mica books. Headings usually are advanced by slabbing to prevent excessive damage to the mica books.

Larger scale open pit methods are used to exploit mica deposits worked solely for the recovery of scrap mica, and also to mine disseminated deposits of mica schist.

PREPARATION FOR MARKET

Preparation of sheet mica for market depends entirely on hand labor. Cobbing and rifting are done with hammers, knives, and fingers; trimming may be done with knives, sickles, shears, or fingers. First, the rough books are cobbed to remove adhering dirt, rock, and defective mica. Next, the cobbed mica is rifted or split into suitable thicknesses, and the major flaws are removed. The products of the rifting operation are classified broadly as untrimmed sheet mica and scrap mica. Trimming, the next step in processing, removes broken and ragged edges, loose scales, and other major imperfections. In the United States, trimming is done with a knife to produce a beveled-edge cut, the preferred type of trim. Care must be taken during rifting and trimming to determine what part of the mica should be removed to result in minimum waste and a sheet with the maximum usable area. The trimmed mica is classified first according to grade (size) and then according to quality. The quality of natural muscovite sheet mica is determined visually. Interpretation of visual standards may vary from one observer to another. After being classified, the trimmed mica is ready to market.

Scrap mica from mining, trimming, or fabricating sheet mica is bagged and sold without further preparation to mica grinders. To recover scrap mica from schist, the rock is crushed and transported, usually with water, to a series of roll crushers and screens. Here the gangue materials pass through the screens, while the mica is washed from the screens and carried to a draining bin from which it is fed by screw feeder to an oil-fired rotary drier. The discharge from the drier is sent to a 14-mesh screen from which the fines go to waste. The oversize is passed through a roll crusher and sent to a dry-grinding operation.

Raw material for dry-ground mica is obtained from mine scrap, from crushing and milling schists, or as a coproduct of kaolin washing or feldspar flotation. Buhr mills, rod mills, high-speed hammer mills all have been used for dry grinding mica. At present, high-speed hammer mills are the most widely used for dry grinding. The mill feed consists of mica that has been washed, screened, and dried. The mill is in circuit with an air separator which returns oversize for additional grinding and discharges the fine material to a screening operation. Various sized fractions are bagged for marketing. The yield of ground mica from beneficiated scrap is usually 95 to 96 percent. A special type of dry-grinding machine, called a Micronizer, produces "micronized" mica. This is an ultrafine material produced in a disintegrator that has no moving parts but depends on jets of high pressure superheated steam to reduce the mica to micron sizes. Micronized mica is produced

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in particle size ranges of 10 to 20 microns and 5 to 10 microns. Another device for dry grinding mica by means of fluid energy is the Majac Mill. Mica is fed continuously from a screw conveyor into a chamber containing two horizontal directly opposed jets. The particle size of the product can be controlled over a broad range down to the micron sizes.

Raw material for wet-ground mica is mainly shop scrap and factory scrap but high-quality mine scrap can be used. Wet-ground mica is produced in mills of the chaser type. Grinding surfaces, which must be such as to preserve the luster or sheen of the mica, usually are made of wood. The type of mill usually employed consists of a cylinder steel tank which is lined with wooden blocks laid with the end grain up. The rollers used are usually wooden, which revolve at 15 to 30 r.p.m. Scrap mica is fed from hoppers to the mill where water is added gradually to form a thick paste. After the bulk of the mica has been ground to the desired size (5 to 8 hours, depending on the feed material), the charge is sluiced from the mill into settling bins where the gritty impurities sink. The mica overflows to a settling tank and is further dewatered by centrifuging and steam drying. The dried product is sized by screening on enclosed multiple-deck vibrating screens, transferred to storage bins, and then bagged for shipment.

MANUFACTURE OF SYNTHETIC MICA

Synthetic mica is manufactured in a furnace which consists of a shell to hold the batch and a pair of graphite electrodes positioned to generate heat in the interior of the batch. A variable transformer controls the supply of alternating-current electricity to the electrodes.

The batch for normal fluorphlogopite consists of a properly proportioned, dry, pulverized, uniform mixture of potash feldspar, potassium silicofluoride, magnesia, alumina, and silica. The batch usually is compounded to have fluorine present in excess of stoichiometric proportions. Although the fluorphlogopite melt is an excellent electrical conductor, the cold batch is a good insulator. Hence, a small-diameter graphite resistor connecting the vertical electrodes is used to start the melting and is consumed by oxidation after several hours of operation but not before a small pool of melt connects the electrodes. Heating is continued until the melt has advanced to within a few inches of the steel shell. Thus, the raw and partially reacted batch remaining around the melt is the container for the melt which has a temperature of about 1,360° C. After the power is cut off, the melt is permitted to cool slowly. After several days, the crystallized melt is broken with pavement breakers, large crystals hand sorted and finer mica crushed, and ground.

USES

Such characteristics as flexibility, resilience, transparency, excellent cleavage, moderate softness, extreme smoothness, vitreous luster, chemical inertness, low electrical and thermal conductivity, tolerance to fairly high temperatures, high dielectric strength, low power-factor losses, and low unit cost make mica usable in many industries and in many diversified applications. Sheet mica, either as single pieces split from crystals or as composite pieces in a built-up form, is an important material in the electronic and electrical industries. The higher qualities of block mica are used principally in the manufacture of electronic tubes, high-temperature steam gage glasses, and regulator diaphragms. Lower qualities of block mica, including punch mica, are used as electrical insulation in household appliances, incandescent lamps, fuse plugs, and other electrical equipment. Film mica is used principally as a dielectric in capacitors, particularly for the electronic industry.

Phlogopite is inferior to muscovite in many electrical properties but replaces muscovite as an electrical insulator where its ability to withstand temperatures up to 1,000° C, compared with 500° C for muscovite, is important.

Data on the end-product uses of muscovite block and film fabricated in 1963 are given in table 3.

Mica splittings are used in the manufacture of sheets of built-up mica. Products cut or stamped from this material are used principally as an insulating material in electric motors, generators, and transformers.

Table 4 gives data on the various products of built-up mica made from splittings in 1963.

Scrap mica is used principally as a raw material for producing ground mica. Dry-ground mica is used in large tonnages as a filler and surface coating for roofing materials, as a filler in wallboard joint cements, and as an ingredient in paints. Smaller quantities are used in numerous products, including rubber, plastics, drilling mud, pipeline enamel, and welding rods. Wet-ground mica is used principally by paint, wallpaper, and tire manufacturers.

Table 5 shows the use pattern for ground mica sold in 1963.

A growing use for scrap mica is in the production of reconstituted mica. Reconstituted mica is used in some applications formerly requiring built-up mica and in electronic capacitors.

TABLE 3.—*Fabrication of muscovite ruby and nonruby block and film mica, by qualities and end-product uses in the United States in 1963*

[Pounds]

Variety, form, and quality	Electronic uses				Nonelectronic uses			Grand total
	Capacitors	Tubes	Other	Total	Gage glass and diaphragms	Other	Total	
Block:								
Good Stained or better	963	33,304	1,784	36,051	6,018	58	6,076	42,127
Stained	4,351	824,787	10,206	839,344	2,716	21,334	24,050	863,394
Lower than Stained [1]	5,533	497,453	31,378	534,364	9,612	744,298	753,910	1,288,274
Total	10,847	1,355,544	43,368	1,409,759	18,346	765,690	784,036	2,193,795
Film:								
First quality	5,390			5,390				5,390
Second quality	60,244			60,244		115	115	60,359
Other quality	2,100			2,100				2,100
Total	67,734			67,734		115	115	67,849
Block and film:								
Good Stained or better [2]	66,597	33,304	1,784	101,685	6,018	173	6,191	107,876
Stained [3]	6,451	824,787	10,206	841,444	2,716	21,334	24,050	865,494
Lower than Stained	5,533	497,453	31,378	534,364	9,612	744,298	753,910	1,288,274
Total	78,581	1,355,544	43,368	1,477,493	18,346	765,805	784,151	2,261,644

[1] Includes punch mica.
[2] Includes First- and Second-quality film.
[3] Includes other-quality film.

TABLE 4.—*Built-up mica [1] sold or used in the United States, by products*

[Thousand pounds and thousand dollars]

Product	1963	
	Quantity	Value
Molding plate	1,143	$2,965
Segment plate	1,214	2,917
Heater plate	524	(2)
Flexible (cold)	602	1,755
Tape	1,441	5,911
Other	83	2,065
Total	5,007	15,613

[1] Consists of alternate layers of binder and irregularly arranged and partly overlapped splittings.
[2] Included with "Other" to avoid disclosing individual company confidential data.

TABLE 5.—*Ground mica sold by producers in the United States, by uses*

Use	1963	
	Short tons	Value (thousands)
Roofing	38,980	$1,370
Wallpaper	1,269	188
Rubber	6,979	728
Paint	23,597	1,890
Plastics	(1)	(1)
Welding rods	1,169	58
Joint cement	24,625	1,603
Well drilling	(1)	(1)
Other uses [2]	20,632	968
Total	117,251	6,805

[1] Included with "Other uses" to avoid disclosing individual company confidential data.
[2] Includes mica used for molded electric insulation, house insulation, Christmas tree snow, annealing, and other purposes.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Feldspar is produced as a byproduct at some sheet mica mines, particularly in New England. Beryl, lithium minerals, and columbite-tantalite sometimes are recovered along with sheet mica. Often the concurrent recovery of two or more pegmatite minerals is necessary for economic exploitation of a deposit. Mica encountered in feldspar mining is recovered as a byproduct. In the recovery of feldspar by flotation and in the processing of kaolin, scrap mica and silica sand are byproducts.

ALTERNATE MATERIALS

Other materials have displaced mica in certain fields; for example, heat-resistant glass in stove windows; sintered aluminum oxide in spark plugs; and glass, paper, and ceramic materials for certain capacitor uses. While mica has not been displaced from many electronic applications, widespread miniaturization of equipment and the use of substitutes where practicable have combined to reduce the quantity of mica needed.

Ceramic electronic tubes are constructed according to entirely different concepts than the common glass envelope tubes and require no mica spacers. The all-ceramic tube will withstand high temperatures, and is expected to last much longer than the electronic tubes commonly used today. Evacuating these tubes and

forming a vacuum-tight seal are troublesome. The technology, at present, is not sufficiently advanced to overcome these and other problems so that ceramic tubes can be mass produced. Although small quantities have been made for special applications, these tubes are primarily in the development stage. Ceramic capacitors use plates or bodies made principally of titanium dioxide with other titanates. Wherever high power factors and large changes in capacitance with temperature can be tolerated, ceramic capacitors are used for low capacitance applications.

Transistors have replaced electronic tubes for many applications. A transistor consists of a small piece of semiconducting material, such as germanium or silicon, contacted by three or more electrodes and sealed in plastic. Transistors require no heater current, operate on low voltages, and are smaller, lighter, and more resistant to shock and vibration than vacuum tubes. Transistors, as presently developed, are limited to operating at temperatures, frequencies, and power levels much lower than those attainable with electronic tubes.

For most uses reconstituted muscovite mica can replace built-up mica made from muscovite splittings, and substitution for a substantial part of phlogopite splittings also could be achieved.

A heat-resistant electrical insulation in the form of sheet made by bonding ground mica with aluminum phosphate, is being used in place of lower qualities of sheet mica in some electrical appliances.

SYNTHETICS

Synthetic micas are true micas that have been prepared by reacting suitable raw materials in the proper proportions. The term synthetic mica often is used loosely at the present time to mean synthetic normal fluorphlogopite. Of all the fluormicas synthesized, only a few thus far have been considered as commercial possibilities, and only normal fluorphlogopite is being produced and used industrially (*1*).

Synthetic mica flake is ground and used in the manufacture of glass-bonded mica. The substitution of synthetic fluorphlogopite mica for natural mica in the glass-bonded material results in an improved product even when low-temperature glasses are used.

RESERVES

No significant domestic reserve of sheet mica has been demonstrated because little exploration is done in advance of mining, and concentrations of mica usually are mined promptly after discovery. The total reserve of muscovite sheet mica is estimated at 4 to 5 million pounds.

Quantitative estimates cannot be made for the reserve of scrap mica because it includes scrap dependent on sheet production, scrap produced directly from pegmatites, and scrap (flake) recovered from disseminated deposits such as mica schist. Resources of scrap mica occurring as small flakes in disseminated deposits are essentially unlimited (*26*).

There are no known domestic reserves of phlogopite mica, although a few occurrences have been reported.

Quantitative information on reserves or resources in foreign countries is unavailable. The major reserves of muscovite are in the Bihar and Madras areas of India and are considered to be very large. Other large reserves are in Brazil, Western Africa, the Rajputana area of India, and the Lake Baikal and Sayan Upland areas of the U.S.S.R. Argentina, Australia, Southern Rhodesia, and the South Enissey Range of the U.S.S.R. have smaller but substantial reserves.

Canada and the Malagasy Republic have the world's major reserves of phlogopite. Additional reserves are available in the Sludyanka River district and Alden area of the U.S.S.R., Ceylon, and Mexico.

SOURCES OF STATISTICAL INFORMATION

Government agencies and trade organizations compile statistics on various aspects of the mica industry. The Bureau of Mines collects statistics semiannually from fabricators of block and film mica and annually from producers of crude mica, from consumers of mica splittings, and from grinders of mica. Data on imports and exports are compiled by the Bureau from monthly data obtained by the U.S. Department of Commerce. World production data are compiled annually by the Bureau from foreign statistical sources. The National Electrical Manufacturers Association and the Wet-Ground Mica Association issue regular releases on transactions by member companies.

Data of the Bureau of the Census, U.S. Department of Commerce, on imports of mica follow the tariff classification, which in many respects differs from trade practices.

PRODUCTION, CONSUMPTION, AND TRADE

The United States leads the world in production of total mica (sheet plus marketable scrap), but the bulk of the product is scrap mica. India, ranking second in total mica pro-

duction, produces principally sheet mica and is the major supplier of this category (table 6).

The United States consumes more sheet mica, principally for electrical insulation, and grinds more scrap mica than any other country (table 7). Muscovite splittings and the lower qualities of muscovite block constitute the largest portion of sheet mica used. Comsumption of ground mica, as indicated by sales, comprises about 85 percent dry-ground materials and 15 percent wet-ground.

India furnished about 82 percent of the total imports of mica film and splittings in 1963 and about 21 percent of block mica. Brazil furnished about 63 percent of all block mica imports. The Malagasy Republic supplied almost all the phlogopite splittings. U.S. mica exports consisted mainly of ground mica.

Tariffs on mica, as described in the "Tariff Schedules of the United States, Annotated (1963)" are shown in table 9.

TABLE 6.—*World production of mica by major producing countries*

[Thousand pounds]

Country	1954-58 (average)	1959	1960	1961	1962	1963
Brazil	3,205	2,553	4,440	9,101	3,885	2,758
Canada	1,594	814	1,701	1,814	1,204	1,069
India (exports)	46,614	51,535	65,514	58,155	68,757	75,121
Malagasy Republic	1,490	2,191	2,229	2,225	2,961	2,128
South Africa, Republic of	5,092	3,761	6,713	5,443	4,903	4,723
United States	180,150	203,788	196,411	198,614	215,767	218,749
Other countries	71,855	85,358	87,992	89,648	92,523	95,452

TABLE 7.—*Consumption of sheet mica in the United States by category*

[Thousand pounds]

Category	1959	1960	1961	1962	1963
Muscovite block and film:					
Good Stained or better [1]	91	78	99	125	108
Stained [2]	1,402	1,188	1,212	1,096	865
Lower than Stained [3]	1,364	1,500	1,218	1,563	1,288
Total	2,857	2,766	2,529	2,784	2,261
Phlogopite block	12	10	15	27	31
Muscovite splittings	6,726	5,915	5,274	6,382	6,406
Phlogopite splittings	497	312	240	346	281

[1] Includes First- and Second-quality film.
[2] Includes other-quality film.
[3] Includes punch mica.

SELF-SUFFICIENCY AND STRATEGIC CONSIDERATION

The United States is not self-sufficient in any category of sheet mica or in high-quality scrap mica.

Historically, sheet mica produced domestically has equaled no more than a small fraction of U.S. requirements for high-quality mica but instead has been principally punch and circle mica. The United States is almost completely dependent on foreign sources for strategic sheet mica. Of the five strategic categories only muscovite block mica has been produced in the United States in significant quantities and then only under the stimulus of above-market prices paid by the Government. Stained and better qualities obtained from processing domestic mica purchased by the Government in 1960 would have furnished 16 percent of the total fabrication of muscovite block and film of these qualities, irrespective of grades. The Government purchase program was terminated in June 1962.

Domestic production during World War II filled approximately 15 percent of the total block and film mica requirement of the United States. However, only 4 percent of the requirement for strategic-quality mica acceptable for stockpiling came from domestic production.

Virtually all mica splittings, the bulk of U.S. consumption of strategic sheet mica, and all mica films must be imported. As discussed in

TABLE 8.—*U.S. imports and exports of mica*

Year	Imports for consumption				Exports, all classes (short tons)
	Uncut sheet and punch (pounds)	Scrap (short tons)	Manufactured (short tons)	Total (short tons)	
1954-58 (average)	1,911,673	6,115	5,150	12,221	4,326
1959	3,220,412	4,644	5,042	11,296	5,102
1960	1,088,021	6,240	4,266	11,050	4,012
1961	852,648	3,024	3,763	7,213	3,799
1962	1,110,739	4,458	5,403	10,416	4,028
1963	1,133,521	8,150	4,353	13,070	4,021

Source: Bureau of the Census.

TABLE 9.—*Mica tariffs*

Description	Duty rate
Mica not manufactured (including split block mica and mica over 0.006 inch thick, not cut or stamped to dimensions, shape, or form) and mica scalings, mica cleanings, and other mica waste and scrap:	
Untrimmed phlogopite from which no rectangular piece over 2 inches long or 1 inch wide can be cut.	5 percent ad valorem.
Waste and scrap valued not over 5 cents per pound:	
Phlogopite	12.5 percent ad valorem.
Other	Do.
Split block mica	Free.
Other	4 cents per pound.
Mica splittings	Free.
Mica, not over 0.006 inch thick, not cut or stamped to dimensions, shape, or form.	Do.
Mica, not over 0.006 inch thick, cut or stamped to dimensions, shape, or form, whether or not perforated or indented, and whether or not dedicated to a specific use:	
Not perforated or indented:	
Fuse disks, split to thickness	25 percent ad valorem.
Other	40 percent ad valorem.
Perforated or indented	25 percent ad valorem.
Mica, ground or pulverized	12.5 percent ad valorem.
Built-up mica	17 percent ad valorem.
Articles not specifically provided for, of mica	25 percent ad valorem.

the section on alternate materials substitutes for mica splittings are closer to realization than for other categories of mica.

GOVERNMENT PROGRAMS

The defense program for mica since World War II has consisted of a purchase program for domestic mica, purchases of imported mica for the strategic stockpile, Commodity Credit Corporation (CCC) barter contracts for the supplemental stockpile, and exploration assistance, initially under the Defense Minerals Exporation Administration (DMEA), and subsequently under the Office of Minerals Exploration (OME).

In 1952 the Government began purchasing domestically produced block, film, and hand-cobbed muscovite mica at above-market prices. This program terminated, after a number of extensions, in June 1962.

The Government, through established importers, purchased mica produced in foreign countries. Each lot conformed to National Stockpile Purchase Specifications. Government inventories on June 30, 1964 are shown in table 10. Nonstockpile grade mica also is stockpiled.

TABLE 10.—*Mica in Government inventories*

[Short tons]

Grade	National strategic stockpile	DPA inventory	CCC stocks	Supplemental stockpile	Total
Muscovite block, Stained and better	3,331	1,323	144	784	5,582
Muscovite film, first and second qualities	598	51	23	51	723
Muscovite splittings	20,020			2,413	22,433
Phlogopite block	9				9
Phlogopite splittings	1,540			993	2,533

PRICES

Because of the wide range of qualities and grades of sheet mica, and because the differences between qualities often are slight, prices are negotiated between buyers and sellers. Duty-paid prices for imported full-trimmed mica in the range of qualities and grades constituting the bulk of the demand are about as follows: Block mica, $1.25 to $43 per pound; film mica, $5 to $24 per pound; and splittings, $0.20 to $4 per pound. Prices paid under the Government's purchasing program for domestic block mica in the equivalent range are $4 to $70 per pound.

During 1963 E&MJ Metal and Mineral Markets quoted prices for punch mica of $0.07 to $0.12 per pound and for North Carolina scrap mica of $30 to $40 per short ton.

Quotations in Oil, Paint, and Drug Reporter, during 1963, were as follows for carlots of dry-ground mica in bags at works in cents per pound: Paint, 100-mesh, 4; plastic, 100-mesh, 4; roofing, 20- to 80-mesh, 3. The same source quoted equivalent prices for wet-ground mica, as follows: Biotite, 6.5; paint or lacquer, 8.25; rubber, 8; wallpaper, 8.75; white, 5 to 10 microns, 8.25.

TAXES

No special taxes are imposed on the mica industry. Producers of mica are granted a depletion allowance of 23 percent on domestic production and 15 percent on foreign production.

RESEARCH

The bulk of the research on natural mica has been related directly to problems posed by the strategic and critical nature of sheet mica. A detailed review on research carried on by industry and government prior to 1960 was published by the Bureau of Mines (*26*).

Research on synthetic mica has been conducted by the Federal Bureau of Mines. Principal efforts were directed toward growing large single crystals, obtaining basic information on nucleation and the liquid state of fluorphlogopite, reconstituting improved inorganic paper from water-swelling compounds, and preparing machineable dielectrics by divitrifying synthetic mica glasses.

The U.S. industry-Government program to develop substitutes for natural mica was directed toward obtaining a suitable sheet material that could be obtained from synthetic mica. Efforts were directed principally toward inorganic bonding of sheets reconstituted from fluorphlogopite flakes and toward improving the properties of films formed from water-swelling micas.

Synthetic mica research sponsored by the U.S. Air Material Command was concluded in 1961. The objective of the program was to develop a commercially feasible technique for producing large area, single crystals of fluorphlogopite mica.

Evaluation of reconstituted natural mica as a substitute for natural mica in electronic tubes and capacitors was sponsored by the U.S. Army Signal Corps, and the Navy Bureau of Ships supported research on the use of synthetic mica for encapsulating electronic components.

OUTLOOK

Domestic production of good qualities and grades of sheet mica was at a high level prior to 1962 owing to the influence of the Government stockpiling program, which purchased sheet mica at a premium price. Expiration of this program in June 1962 caused a sharp reduction in production during 1962 and the following year. This reduction will probably continue until only a nominal quantity is produced annually.

Domestic sheet mica (block, film, and splittings) requirements will continue to be met largely by imports of muscovite from India and phlogopite from the Malagasy Republic. This pattern will continue unless interrupted by international conflict or the development of acceptable synthetic mica substitutes.

Action by the Indian Government early in 1964 establishing minimum prices for splittings and other types of mica may result in lower Indian mica production because fewer purchasers may be willing to pay the increased price. Any inability of Indian producers to find buyers may cause smaller and less efficient mining operations to be curtailed. If production decreases and price increases are maintained, major users may commence expanded efforts to find suitable substitutes for Indian mica in many industrial uses.

Consumption of the higher qualities of muscovite block and film during the next few years is expected to continue at the 1963 level. Continued demands of the expanding electronics industry will require block mica for the fabrication of electronic tubes and film mica for condensers.

The demand for built-up micas should increase slowly, at a rate dependent on the economics of the materials, technical improvements in reconstituted mica products, and the conversion of design engineers to the use of reconstituted material.

Ground mica production since 1961 has shown a strong pattern of increase which will probably continue. Increased consumption for roofing materials and paints can be expected as the building construction industry expands with the growing population. Other industries, such as plastics, welldrilling, welding, and rubber, also will continue to require ground mica. Substantial expansion of ground mica consumption will depend on the development of new uses.

PROBLEMS

SHEET MICA

A serious problem is the insufficient domestic supply of sheet mica that forces the United States to rely on distant and uncertain foreign sources to supply most of its requirements.

The inadequate market for the more plentiful classes of mica—block and film of the lower qualities, splittings, and scrap—and the impracticability of recovering and selling other pegmatite minerals hinder the development and exploitation of domestic mica deposits in particular. Lack of coproducts to share the costs of mining and recovery increases the cost and possibly decreases the supply of the higher qualities of block and film mica. The problem is accentuated by increasing demands for higher qualities and larger sizes of sheet mica and by partial displacement of more plentiful classes by other materials.

Numerous mining and processing problems result from the manner in which mica occurs. The often irregular distribution of mica in pegmatites complicates estimation of reserves. The necessity of recovering undamaged books of mica and the softness of the material create special rock-breaking problems. Large quantities of rock must be mined for each pound of usable sheet mica recovered which burdens the economics of the operation.

The large amount of skilled hand labor required to produce and qualify block, film, and splittings makes preparation of sheet mica uneconomical in the United States. This labor factor in combination with inadequate domestic resources prevents development of a mica processing industry that could serve as a base to overcome U.S. dependence on foreign sources of mica in wartime.

The lack of an accurate relation between the properties required in end-use applications of sheet mica and the specifications for visual quality of block and film mica may result in some unnecessary use of the highest qualities and failure to utilize all satisfactory lower qualities. The problem is made more difficult by the absence of practical, reproducible, scientific tests to evaluate sheet mica for specific end uses.

The lack of satisfactory bonding techniques is the major obstacle to using synthetic mica flake to produce a sheet material having suitable electrical and mechanical properties. The use of single crystals of synthetic mica in elec-

tronic applications is hindered by the present inability to obtain large crystals of synthetic mica with an orientation and yield that permit economic recovery.

SCRAP MICA

Greatly expanded production of reconstituted natural mica will be hindered by the lack of sufficient known supplies of suitable high-quality muscovite scrap mica.

Since scrap mica goes principally into the production of ground mica, the problems of the two are virtually inseparable. Ground mica for some uses, especially fillers, is subject to displacement by other materials unless more economical methods of recovering and grinding scrap are developed.

The lack of markets for scrap and ground mica, particularly of the lower qualities, creates a problem in utilizing all that can be produced readily.

The lack of standard specifications for ground mica deters the development of new markets and complicates the reduction of costs for grinding scrap.

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MOLYBDENUM

By R. W. Holliday [1]

FIRST isolated as a metal in 1782, molybdenum was not used widely until the early years of the 20th century when it played a role in commercial development of the electric lamp. Later, during and after World War I, it became an important constituent of alloy steel.

A single mine, the Climax mine in Colorado, has produced more than half of the world molybdenum supply from 1925 to the present and the free world resource is predominantly in the Western Hemisphere.

Molybdenite (MoS_2) is the principal commercial mineral of molybdenum. Most production is from ores containing only a few pounds of molybdenite per ton. In the United States in 1963 byproduct molybdenite from copper and tungsten mines comprised 27 percent of the total output. Most of the remaining 73 percent came from the Climax molybdenum mine.

All molybdenum ores, including the byproduct ores, are concentrated by flotation. Virtually all of the concentrate is roasted to molybdic oxide. This oxide is added directly to steel and other alloys or it is converted to other products.

The known domestic reserve, of ores that are commercial under present conditions, is estimated to comprise a 37-year supply averaging 50,000 tons per year of contained molybdenum. However, the rate of growth in the industry during recent years indicates that annual requirements for consumption and export may exceed 50,000 tons by 1972.

BACKGROUND

The mineral, molybdenite, was identified as a sulfide of molybdenum in 1778 and the metal was isolated in 1782. More than 100 years later, in 1893, a 96-percent pure metal was produced and in the following year production of a molybdenum-bearing armorplate was reported (*6, 8*).[2] Commercial use as an alloy constituent of steel was announced prior to 1905 but the first real stimulus to its use in alloys came in the First World War when shortages of other alloying elements centered interest on molybdenum. Wide spread search for deposits, development of a flotation process for separating molybdenite from its ores, and applications research followed. Beginning about 1920, there was rapid growth in production and use.

Methods for producing ductile molybdenum metal in the form of wire, rod, and sheet by powder metallurgy techniques were developed in the years following 1907. The metal was an important factor in development of the electrical and more recently the electronics industries. Molybdenum has also been used for many years in chemicals and dyes.

Small quantities of molybdenum ore were mined in Norway about 1880. Australia and the United States were producing by 1900. Canada was a prominent producer in the years 1916–19.

The Climax deposit in Lake County, Colo., and the Questa deposit in Taos County, N. Mex., were among those exploited during the First World War, and by 1925, these two deposits were the source of about 75 percent of the world supply of molybdenum. In succeeding years as demand for molybdenum in making ferrous alloys and other uses grew rapidly, the Climax mining and milling facilities were expanded because the large disseminated deposit proved amenable to large-scale mining. The Questa vein deposit was not mined on a large scale and consequently, annual output from that source never exceeded more than a few hundred tons of molybdenum. However, at the end of 1963, mine and concentrating plant were being readied for production of 5,000 tons per year of molybdenum in concentrate from a large new low-grade deposit at the Questa property.

In 1933, the Greene Cananea Copper Co., a Mexican subsidiary of The Anaconda Company, started separating molybdenum from copper concentrate made from the sulfide ores of the

[1] Commodity specialist.
[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

Colorada deposit at Cananea. Molybdenum-bearing copper ores have since become an important source of molybdenum, and in recent years about one-third to one-half of the world annual output has been obtained as a byproduct of copper, largely from deposits in the United States, the U.S.S.R., and Chile.

World molybdenum production increased almost continuously from 500 tons in 1925 to 34,500 tons in 1943. Output declined to 11,500 tons in 1946, but rose to a peak of 45,800 tons in 1963.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

World production of molybdenum in concentrate was estimated at 45,800 short tons in 1963. Of this total the United States produced 71 percent; the U.S.S.R. produced 14 percent; Chile produced 7 percent; China produced 4 percent; Peru 1; Canada 1; and five other countries together produced the remaining 2 percent.

Ores containing molybdenum as the principal value accounted for more than 70 percent of the domestic output in 1963 and byproduct sources produced nearly 30 percent. Unconfirmed data suggest that about 50 percent of the U.S.S.R. production was from copper-molybdenum ores, about 30 percent from molybdenite ores, and about 20 percent from tungsten-molybdenum ores. Nearly all of the Chilean and Peruvian output was a byproduct of copper production.

Principal U.S. producers of molybdenum concentrate and producers of molybdenum products are listed in table 1. Of the producers of molybdenum concentrate, Climax Molybdenum Co., Division of American Metal Climax is by far the largest. This firm, from a single mine at Climax, Colo., produced more than half of the world output between 1925 and 1963. In 1963 Climax produced 73 percent of the U.S. total. The firm also operates plants in Michigan and Pennsylvania for converting concentrate to products including ingots, billets, and other mill products and research laboratories in Michigan.

The Molybdenum Corporation of America has been a leading producer of molybdenum products for many years. A plant at Washington, Pa. produces molybdic oxide and ferromolybdenum. A plant at York, Pa. produces molybdenum chemicals. The firm has operated molybdenum mines at various times over many years, but the first large-scale operation is scheduled for initial production at the Questa deposit in 1965. Current plans call for an output of about 5,000 tons of molybdenum in concentrate, per year.

Duval Corp. and Union Carbide Nuclear Co. produce byproduct molybdenite and convert the concentrate to molybdic oxide.

Kennecott Copper Corp. is the largest byproduct producer of molybdenite. The company recovers molybdenum in concentrate at its Arthur and Magna copper concentrating plants near Salt Lake City, Utah, and at Chino mines, Hurley, N. Mex., and Nevada mines, McGill, Nev. The firm also controls Braden Copper Co. which is a major producer of molybdenum in Chile.

Virtually all domestic producers of concentrate, except exporters, ship to one of the producers of molybdic oxide listed in table 1.

Annual productive capacity in Colorado is expected to increase some 5,000 tons by 1967 or 1968 through expansion at Climax and development at the company's Urad deposit in Clear Creek County. Annual capacity in New Mexico is expected to increase 5,000 tons by the end of 1965 from the Questa mine; and in Arizona 1,500 tons from copper mines.

The largest foreign, free world producers are Chile Exploration Co., Andes Copper Mining Co., both subsidiaries of Anaconda, and Braden Copper Co., a subsidiary of Kennecott; all in Chile. Southern Peru Copper Corp. began producing byproduct molybdenite in 1962 and produced more than 500 tons of molybdenum in concentrate in 1963. Planned development will increase Canada's annual production from about 500 tons in 1963 to perhaps 8,000 tons within the next several years.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Molybdenite (MoS_2) is the chief commercial molybdenum mineral occurring, usually disseminated in small quantities, in a host rock. Molybdenite concentrate is the mineral after separation from other constituents in the crude ore. Industry specifications for the concentrate vary widely although a 95-percent MoS_2 content is a usual basis for price quotations. National Stockpile Specification P–74–R5, dated July 15, 1963, listed the following chemical requirements for molybdenite concentrate:

		Percent by weight (dry basis) [1]
Molybdenum disulfide (MoS_2)	minimum	90.00
Copper (Cu)	maximum	.45
Lead (Pb)	do	.15
Phosphorus (P)	do	.04
Tin-plus-arsenic (Sn+As)	do	.15

[1] The free moisture content shall not exceed 4 percent.

TABLE 1.—*Principal U.S. producers of molybdenum concentrate and molybdenum products*

Company	Mine or mill site	Processing plant site	Major product
American Metal Climax, Inc.:			
Climax Molybdenum Co	Climax mine, Lake County, Colo.		Concentrate (MoS_2).
Climax Molybdenum Company of Michigan.		Coldwater, Mich	Metal powder.[1]
Climax Molybdenum Co		Langeloth, Pa	Molybdic oxide, ammonium molybdate, ferromolybdenum, sodium molybdate, purified disulfide.
American Smelting and Refining Company	Silver Bell mine, Pima County, Ariz.		Concentrate (MoS_2).
Do	Mission mine, Pima County, Ariz.		Concentrate (MoS_2). (Initial operation of molybdenum recovery unit scheduled for 1964).
Bagdad Copper Corp	Yavapai County, Ariz		Concentrate (MoS_2).
Duval Corp	Esperanza mine, Pima County, Ariz.	Mine site	Concentrate (MoS_2), molybdic oxide.
Do	Ithaca Peak mine, Mohave County, Ariz.		Concentrate (MoS_2). (Initial operation scheduled for 1964).
Fansteel Metallurgical Corp		North Chicago, Ill	Metal powder.[1]
General Electric Co.:			
Lamp Metals and Components Department.		Cleveland, Ohio	Ammonium molybdate, metal powder.[1]
Do		Dover, Ohio	Metal powder.[1]
Inspiration Consolidated Copper Co	Inspiration mine, Gila County, Ariz.		Concentrate (MoS_2).
Kennecott Copper Corp.:			
Chino Mines Division	Grant County, N. Mex		Do.
Nevada Mines Division	White Pine County, Nev		Do.
Utah Copper Division	Salt Lake County, Utah		Do.
Magma Copper Co., San Manuel Division	Pinal County, Ariz		Do.
Molybdenum Corporation of America		Washington, Pa	Molybdic oxide, ferromolybdenum.
Do		York, Pa	Molybdic oxide, ammonium molybdate, sodium molybdate.
Do	Questa mine, Taos County, N. Mex.		Concentrate (MoS_2). (Initial production from new plant scheduled for 1965).
M & R Refractory Metals Inc		Springfield, N.J	Metal powder (pellets), self-reducing molybdenum mix.
North Metal and Chemical Co		York, Pa	Sodium molybdate.
Phelps Dodge Corp., Morenci Branch	Greenlee County, Ariz		Concentrate (MoS_2).
Philips Elmet Corp		Lewiston, Maine	Metal powder.[1]
Republic Steel Corp		Canton, Ohio	Molybdic oxide.
SW. Shattuck Chemical Co		Denver, Colo	Molybdic oxide, ammonium molybdate, calcium molybdate, sodium molybdate.
Southern California Chemical Co		Los Nietos, Calif	Calcium molybdate.
Sterling Drug Company, Inc., The Hilton Davis Chemical Co. Division.		Cincinnati, Ohio	Sodium molybdate.
Sylvania Electric Products, Inc., Chemical and Metallurgical Division.		Towanda, Pa	Ammonium molybdate, metal powder (pellets).[1]
Union Carbide Corp., Nuclear Division	Pine Creek mine, Inyo County, Calif.	Mine site	Concentrate (MoS_2), molybdic oxide.
Universal Cyclops Steel Corp		Bridgeville, Pa	Metal powder.[1]
Vick Chemical Co., subsidiary of J. T. Baker Chemical Co.		Phillipsburg, N.J	Molybdic oxide, ammonium molybdate, sodium molybdate, molybdic acid.
Wah Chang Corp., Glen Cove Division		Glen Cove, Long Island, N.Y.	Molybdenum pellets, molybdenum spray powder, molybdenum carbonyl, metal powder.[1]
Do		Albany, Oreg	Metal powder.[1]
Westinghouse Electric Corp		Bloomfield, N.J	Do.[1]

[1] Produces wire, rod, sheet, or other mill products.

A purified molybdenite concentrate that contains more than 99.9 percent MoS_2 is required for use in manufacturing molybdenum disulfide lubricants.

Technical molybdic oxide (MoO_3) is produced by roasting molybdenite concentrate in air. It is used as a raw material for producing all types of molybdenum chemicals, for manufacturing ferromolybdenum, and for adding molybdenum to iron and steel alloys.

Specification P–74–R5 lists the following chemical requirements for technical grade molybdic oxide:

		Percent by weight (dry basis) [1]
Molybdenum (Mo)	minimum	60.00
Copper (Cu)	maximum	.50
Lead (Pb)	do	.15
Phosphorus (P)	do	.05
Sulfur (S)	do	.25

[1] The free moisture content shall not exceed 0.5 percent.

Purified molybdic oxide is produced from the technical grade by sublimation or by chemical means. It is used as a raw material for producing molybdenum metal powder, chemically pure molybdenum salts and compounds, and in special alloys.

Ferromolybdenum is a molybdenum-iron alloy produced in the electric furnace or by a thermite process. It is used to introduce molybdenum into iron or steel alloys and as a coating material on welding rods.

Specification P–74–R5 lists the following chemical requirements for ferromolybdenum:

		Percent by weight (dry basis)	
		Grade A	*Grade B*
Molybdenum (Mo)	minimum	60.00	60.00
Carbon (C)	maximum	2.50	.10
Carbon (C)	minimum	2.00	-----
Copper (Cu)	maximum	.50	.50
Phosphorus (P)	do	.10	.10
Silicon (Si)	do	1.00	1.00
Sulfur (S)	do	.20	.20

Molybdic oxide briquettes and calcium molybdate are other forms used for adding molybdenum to alloys.

Ammonium molybdate, as well as purified molybdic oxide, is used for the production of molybdenum metal powder and for various chemicals, fertilizers, and catalysts. Sodium molybdate is used in the production of fertilizers, pigments, and chemicals.

Molybdenum metal powder is used for production of substantially pure molybdenum mill products. It may also be used for adding molybdenum to special alloys.

TECHNOLOGY

Mineralogy and Geology

Molybdenite is the disulfide of molybdenum, containing about 60 percent molybdenum and 40 percent sulfur. Its specific gravity is 4.6 to 4.7 and it resembles graphite in appearance and softness. Its streak is bluish grey on paper and greenish grey on porcelain. Molybdenite yields sulfur fumes when ignited on charcoal. It occurs in pegmatites, aplites, contact metamorphic zones, quartz veins of the single-vein type, porphyry copper deposits, and in stockworks composed of myriads of intersecting veinlets.

The most important discovery to date, the stockworks at Climax, Colo., was formed by intrusion of a quartz-monzonite magma into granites, schists, and porphyry; solidification and fracturing of the quartz-monzonite and the surrounding granite and schist; injection of quartz-monzonite dikes, some of which contained molybdenite; and hydrothermal deposition of quartz, orthoclase, molybdenite, pyrite, and sericite. The hydrothermal solutions penetrated the smallest fractures depositing quartz-molybdenite veinlets that make the rock look like a breccia (*10*).

Quartz veins with molybdenite are widely distributed and two deposits of this type have yielded significant quantities of molybdenite. The Questa deposit in New Mexico and the La-Corne deposit in Quebec both produced consistently over many years. (A large, low-grade occurrence adjacent to the Questa deposit is similar to the Climax formation in that hydrothermal solutions deposited a network of quartz-molybdenite veinlets in a previously fractured and shattered rock complex.)

Most of the porphyry coppers in the Western United States contain small quantities of molybdenite disseminated, with the copper minerals, through large bodies of granitic rock.

Contact-metamorphic skarn or tactite zones containing some molybdenite or powellite are relatively common. Pine Creek mine, near Bishop, Calif., has produced molybdenum as a byproduct of tungsten since 1939.

Pegmatite and aplite with small quantities of molybdenite, are found throughout the world, but no appreciable production has resulted.

Molybdenum oxide minerals have yielded molybdenum, but production has been relatively insignificant. Wulfenite ($PbMoO_4$) is a secondary mineral formed in the oxidized zones of lead- and molybdenum-bearing deposits. Composition of the mineral is variable in that tungsten substitutes for molybdenum and calcium for lead. Powellite ($CaMoO_4$) is an alteration product of molybdenite, frequently associated with scheelite and containing up to 10 percent tungsten trioxide. Ferrimolybdite (long known as molybdite) and Ilsemannite are secondary oxidation products of molybdenite.

Mining

The caving method employed at the Climax mine produced 35,500 tons of ore per operating day in 1963. Essentially the ore body is undercut to induce caving of the ore, which flows by gravity through finger raises into concrete lined scraper drifts. The ore is then scraped into cars on the haulage level. The caving must be carefully controlled to avoid ore dilution and to prevent damage to mine openings.

The smaller vein-type deposits are mined by shrinkage, cut-and-fill, or other conventional methods adapted to existing conditions. The new development at the Questa deposit will employ open-pit methods. The Climax mining method was described in a Bureau of Mines publication (*6*).

Beneficiation

Ores containing molybdenite as the chief valuable mineral and copper sulfide ores containing byproduct molybdenite are beneficiated by flotation. Tungsten ores containing both molybdenite and powellite are beneficiated by a combination of flotation, tabling, and chemical extraction. Complex wulfenite-bearing ores can be concentrated by either gravity or flotation methods, but smelting, leaching, and precipitation are necessary to separate molybdenum from lead and other valuable metals (*6*).

The Climax flowsheet involves crushing, grinding, classification, and a preliminary flotation that produces a rougher concentrate of 8 to 10 percent MoS_2. Tailings from the rougher flotation are routed to the byproduct plant where Humphreys spirals and flotation cells produce a pyrite concentrate that is marketed and tailings that are further treated by tabling and magnetic separators to produce tungsten concentrate and tin concentrate.

The 8- to 10-percent rougher concentrate is

cleaned in additional flotation stages, with grinding and classification between stages, to produce the final concentrate.

Molybdenite is recovered from copper ores containing as little as 0.2 pound MoS_2 per ton.

Copper plants designed to recover molybdenum as a byproduct first produce a concentrate containing both copper sulfide minerals and molybdenite. Methods for separating molybdenite from the copper sulfide minerals and other impurities such as iron sulfides and gangue material in this concentrate vary in detail from producer to producer, but all employ selective flotation. At some plants the molybdenite in the first flotation concentrate is depressed along with some copper and iron sulfide and gangue material, producing a copper concentrate and a tail product that is the rougher molybdenite product. This tail material is filtered and given a light roast to tarnish the copper sulfide minerals before further processing. In other processes the first flotation concentrate is treated by adding lime and steaming to retard the copper sulfide so that a rougher molybdenite concentrate is produced during the second flotation. In either process the molybdenite materials are further cleaned through several conditioning reflotation steps, in which various reagents may be used to effect selective flotation. Recovery of molybdenite varies with the tenor of the crude ore and with the nature of the mineralization and ranges from about 15 to 80 percent.

A hydrometallurgical process for recovering molybdenum from oxidized ores was undergoing pilot plant tests in 1963 at Climax research facilities. Oxidized ores will not be a major source of molybdenum in the foreseeable future, but recent advances in recovery procedures indicate that they will be a significant increment of supply.

Manufacture of Molybdenum Products (*5, 7*)

The principal molybdenum products and their relationships to end uses are shown in figure 1.

Lubricant-grade molybdenum disulfide (MoS_2) is prepared by removal of silica and other impurities from the commercial-grade concentrate. Screening, grinding, leaching, volatilization, washing, and possibly other methods are employed, primarily for extraction of abrasive materials.

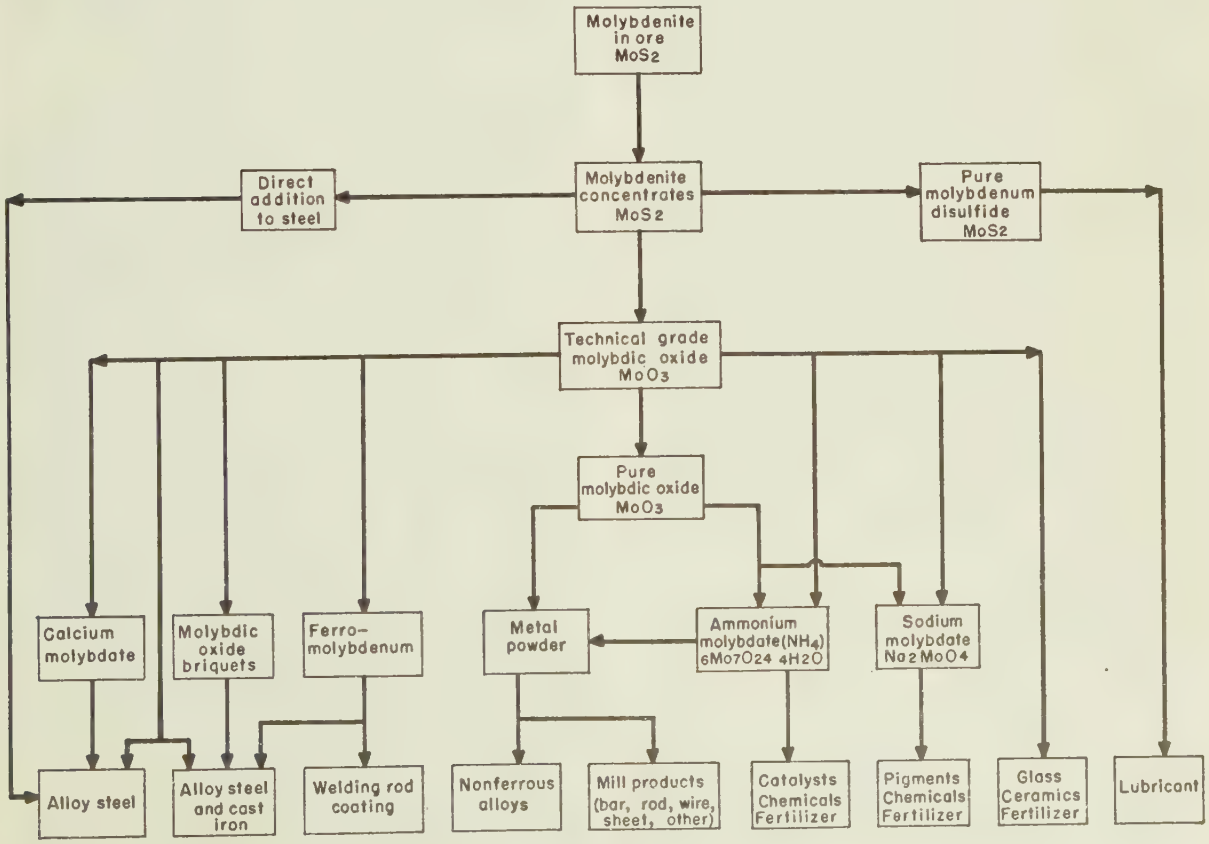

FIGURE 1.—Principal Molybdenum Products and Their Relationships to End Uses.

Technical-grade molybdic oxide is produced by roasting molybdenite concentrate. As the only purpose of the roast is to convert the sulfide, MoS_2, to an oxide, MoO_3, the oxide contains virtually all of the impurities present in the original concentrate. Usual practice is to roast the molybdenite concentrate in multiple hearth furnaces, operated on a heat gradient ranging from about 300° F on the drying to 1,250° F on the roasting hearths. The sulfur dioxide is discharged into the air. For some uses, the molybdic oxide is purified by sublimation or chemically to yield a product of about 99.95 percent MoO_3.

Molybdenum metal powder is produced by the hydrogen reduction of purified molybdic oxide or ammonium molybdate. (Ammonium molybdate is the purest commercially available molybdenum compound. It is produced by dissolving purified oxide in ammonium hydroxide. The solution is then filtered and evaporated, crystallizing out the pure compound.) For fabrication by powder metallurgy methods, the metal powder is compacted into ingots or bars and sintered in a vacuum or a hydrogen atmosphere. Smaller ingots are sintered by resistance heating but large ingots, up to several hundred pounds, are sintered by radiation or induction heating. The sintered piece is further shaped by hot rolling, swaging, or forging.

For larger ingots an arc casting procedure has been in use since about 1945. The process comprises vacuum or inert-gas arc melting in a water-cooled copper mold. The melting takes place in an arc, which operates between a consumable molybdenum electrode and a pool of liquid metal in the mold. Ingots weighing more than a ton can be produced in this way for subsequent extrusion, rolling, or forging (*1*). The consumable electrode is a product of powder metallurgy composed of molybdenum powder, a deoxidizing agent (usually carbon), and sometimes alloying additions.

Two grades of ferromolybdenum are produced, high-carbon and low-carbon. The high-carbon ferromolybdenum is produced in electric furnaces from a charge, consisting typically, of 900 pounds of technical grade molybdic oxide, 200 pounds of iron, 100 pounds of coal, and 160 pounds of lime (*8*).

Low-carbon ferromolybdenum is made either by the aluminothermic or the silicothermic reduction of molybdic oxide.

USES (*3, 6, 8, 9*)

Of the molybdenum consumed in 1963 in the United States, 69 percent was used in alloy steels, 14 percent was used in alloy cast iron and steel mill rolls, 4 percent in high-temperature alloys, 4 percent as metal, and 9 percent in chemicals and miscellaneous applications.

Molybdenum enhances the properties of steel both from its effect in solid solution in ferrite and from its effect in the carbide phase. Low-alloy steels designed for use without heat treatment frequently contain 0.10 to 0.25 percent molybdenum to increase the strength of the steels. Heat treatable low-alloy steels in most instances contain 0.10 to 1.50 percent molybdenum to promote uniform hardness and strength and to reduce softening on tempering at about 1,000° F, to increase strength and creep resistance at elevated temperatures, to reduce brittleness after tempering, and to retard embrittlement in those steels subjected to stress at temperatures of 600° to 1,000° F. Most of these heat treatable low-alloy steels contain less than 0.5 percent molybdenum, often with chromium, nickel, or both, but those designed for moderately high-temperature service often contain more than 0.5 percent molybdenum. Some corrosion-resistant austenitic stainless steels contain 2.0 to 3.0 percent molybdenum to enhance chemical resistance and class A type high-speed steels contain 5.0 to 9.0 percent molybdenum. In the latter steels molybdenum increases hardness and strength at the high operating temperatures developed during cutting operations.

Small additions of molybdenum to cast iron improve its tensile and impact strength, hardenability, and resistance to chipping.

Molybdenum metal has long been used by the electrical industry and more recently in electronics. It is used as filament supports and as mandrels for winding coiled tungsten filaments. Anodes, grids, shields, cathodes, glass-metal joints, and structural parts of electronic tubes employ molybdenum. Electric furnace heating elements, electrical contacts, and electrodes are made of molybdenum metal or molybdenum base alloy.

The missile industry uses molybdenum in high-temperature applications such as nozzles, leading edges, and numerous structural parts.

In the metalworking industry a wide range of uses includes boring bars, hot-work tools, resistance-welding electrodes, molds, thermocouples, and injection molding equipment.

Electrodes for use by the glass industry, weighing 25 to 50 pounds each, comprise an important use for molybdenum.

The nuclear-energy and the chemical industries require molybdenum for tubing, heat exchangers, heat shields, and structural parts.

Sprayed molybdenum has gained importance as a coating for surfaces subject to frictional wear such as shaft bearings and crankshafts.

A potential for growth in the use of molyb-

denum base alloys has emerged during the last decade with advances in fabricating procedures. A 70-percent molybdenum-30 percent tungsten alloy, for example, has been widely adopted by the zinc die casting industry for injection nozzles. One report indicated a life 50 times longer than that of hot-work or high-speed steels. TZM, a molybdenum-0.5 percent titanium-0.08 percent zirconium alloy is also one of the more promising materials of construction for high-temperature use. Growing use of molybedenum-rhenium alloys is due to improved ductility without significant loss of molybdenum's desirable high-temperature characteristics.

Molybdate chrome orange is a pigment used in paints, printing ink, and plastics. Molybdenum catalysts are used in reforming and desulfurizing of petroleum, in hydrogenation of coal, and in other processes. They are effective in reactions involving oxidation, hydrogenation, dehydrogenation, isomerization, cyclization, chlorination, dehydration and condensation, polymerization, and alkylation. Molybdenum disulfide, added to lubricating oils and greases, is widely used in applications requiring superior performance.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Principal byproducts of molybdenum are tungsten concentrate, pyrite, cassiterite, bismuth, and rhenium-bearing materials. The first three are produced at the Climax mine; bismuth is recovered at the LaCorne mill in Canada; and rhenium is recovered from the flue dust collected at some molybdenite conversion plants. Minute quantities of monazite and topaz occur in the Climax molybdenum deposit. These have not been recovered in commercial quantities but some research has been directed toward their recovery.

About 27 percent of the domestic molybdenum concentrate production in 1963 was from copper and tungsten mines. However, expansion at the Climax and Questa mines will reduce the future percentage of the byproduct component.

Tungsten concentrate produced from ores of many deposits contains molybdenum in varying quantities up to about 3 percent as an impurity. Some of this concentrate is used in high-speed steel when the molybdenum is desired, but for some other uses of tungsten, molybdenum is a harmful impurity.

ALTERNATE MATERIALS

There has been little, if any, direct substitution of other metals for molybdenum. Molybdenum is usually considered an alternate material to replace tungsten and other ferroalloy metals in some uses rather than as a metal for which others can be substituted. Molybdenum can replace tungsten in certain high-speed steels, and the reverse is technically feasible, but costs usually favor molybdenum. Boron steels may be used to a limited extent to replace molybdenum-bearing steels where hardenability is the only alloying effect desired. Chromium and manganese could also be substituted for molybdenum to impart hardenability.

Vanadium is also a potential substitute for molybdenum in some steels.

Composite materials, exemplified by the use of a thin molybdenum coating sprayed on piston rings to impart wear resistance, in a sense, can be classed as substitute materials. Honeycomb cores, laminations, fiber reinforced materials, and numerous other composites either replace molybdenum or reduce the quantity that might otherwise be used.

SECONDARY SOURCES AND RECOVERY

Molybdenum, high-speed steels, low-alloy molybdenum-bearing steel, and commercially pure molybdenum scrap are the major sources of secondary molybdenum, but data on the quantities recovered annually are not available. Molybdenum in high-speed steel scrap is reused in making high-speed or other types of tool steels. However, much of the low-alloy scrap goes into carbon steel melts where the molybdenum is diluted and lost to the secondary supply. This loss is due primarily to costs involved in the identification of the alloying elements in such scrap and to the cost of segregating scrap to eliminate contamination.

Relatively pure molybdenum scrap is an important source of molybdenum for nonferrous-molybdenum-bearing alloys, but the quantity of this scrap comprises only a small part of the total secondary molybdenum supply.

RESERVES

Much of the known world molybdenum resource is in the United States, but molybdenum mineralization is widespread and erratic. Many deposits in various parts of the world have not yet been fully explored, because molybdenum is relatively new in its role as an important industrial material. Furthermore, abundant supply from a single, large producer and a number of low-cost byproduct producers undoubtedly has slowed prospecting and exploration until recent years. Continued growth in

demand, however, has stimulated interest and investment, marking the present decade as one of significant expansion.

The known, commercial U.S. molybdenum reserve exceeds 1.5 million tons and potential sources may contain as much as 3 to 5 million tons additional. Proven ores at Climax, Colo., contain 1 million tons of molybdenum; copper and tungsten deposits may contain as much as 350,000 tons of byproduct molybdenum; other deposits under active investigation or development (including the Questa, N. Mex., and the Urad, Colo., deposits) may contain 500,000 or more tons of molybdenum depending on the cutoff grade used for classifying ore.

Domestic resources therefore can be expected to yield 1,850,000 tons of molybdenum from deposits that are now being mined or investigated. As a basis for comparison, this reserve can be regarded as a 37-year supply at an average annual output of 50,000 tons. Domestic production in 1963 totaled 32,500 tons.

Known molybdenum occurrences in Alaska, Arizona, Colorado, Montana, Nevada, New Mexico, North Carolina, and Washington; inferred reserves at operating mines; molybdenum in vanadiferous shales in Idaho, Montana, Utah, and Wyoming; molybdenum-bearing uranium ores in several States; and uranium-bearing lignite in the Dakotas provide reasonable assurance that more than 5 million tons of molybdenum are contained in domestic resources.

About 700 molybdenum occurrences are known in Canada, but few have been productive to date (*11*). Prior to 1963, production exceeded 500 tons only in 1944. Recent exploration has increased the known reserve sufficiently to justify new mine development, but no firm estimate of the total resource is available. Announced developments are expected to increase annual molybdenum output from about 500 tons in 1963 to as much as 8,000 tons in the next 2 to 4 years. Assuming that a minimum 10 year operation is needed for amortization the commercial reserve must contain at least 80,000 tons. One recent estimate suggests 250,000 tons (*5*).

Chile has the largest free world reserve (*9*) outside of the United States. The major portion is in porphyry-copper deposits although a number of small higher grade occurrences are known. Three large copper mines, El Teniente, Chuquicamata, and El Salvador, with some 2.0 to 2.5 billion tons of ore contain some 400,000 or more tons of byproduct molybdenum.

Three large deposits in Peru, the Toquepala, the Quelleveco, and the Cuajone contain minable reserves of copper ore exceeding 1 billion tons. One of these began producing byproduct molybdenum in 1962 and together they may contain 50,000 to 100,000 tons of molybdenum.

Other free world sources with production in 1963 are in Japan, Norway, Mexico, Republic of Korea, and the Philippines. Occurrences of varying potential are known in Turkey, Greenland, Yugoslavia, Australia, and other countries.

Although confirmation and detailed descriptions are lacking, there is little question that the U.S.S.R. molybdenum resource is substantial. More than 100 deposits are known and Russian writers have stated that the reserve is second only to that of China. Reserves in the Soviet Union may approach 1 million tons of contained molybdenum in ores of various economic grades. However, a large part of this total cannot readily be exploited at the present time for geographic and economic reasons.

A 1959 report indicated that 46.2 percent of U.S.S.R. output came from copper-molybdenum ores; 33.2 percent from molybdenite ores; 17 percent from tungsten-molybdenum skarns; and the remainder from miscellaneous types.

Reports of large deposits in mainland China have been published in recent years. However, claims that China has the largest molybdenum resource in the world are not supported by credible data. The Yang-Chia-Chang-Tzu mine in western Liaoning Province, in Manchuria, was estimated, in 1939, to have 8 million tons of ore containing 8 pounds of molybdenum per ton. This and other large deposits in which molybdenum is associated with copper, lead-zinc, or tungsten undoubtedly comprise a large potential. The Chinese claim that extensive molybdenum deposits have been discovered in the Chiń-ling (Tśin-ling) Mountains somewhere in Shensi and Honan Provinces.

CONSERVATION PRACTICES IN PRODUCTION AND USES

Mining and concentrating efficiency permit the exploitation of ores containing only a few pounds of molybdenite (MoS_2) per ton as the major commercial mineral. Some byproduct producers recover molybdenite from ores containing only fractions of a pound per ton. A new unit to recover molybdenum from oxidized ores is scheduled to begin operation at Climax in 1966. Commercial recovery of byproduct molybdenum from uranium ores was reported in 1963.

Recovery exceeds 91 percent of the molybdenite contained in crude ore treated at Climax. Recovery from the copper ores is much lower because of the very low content in the crude ores, but in some instances is estimated as high as 80 percent. Recovery of molybdenum from concentrate at conversion plants is on the order of 99 percent. Molybdenum-bearing scrap is an important source of molybdenum although

much of the molybdenum used in low-alloy steel is lost.

Rhenium is recovered as a byproduct from the flue dust of some molybdenite concentrate roasting plants but the process is costly and, therefore, not economic for all plants.

SOURCES OF STATISTICAL INFORMATION

In the United States, data on production, shipments, consumption, and stocks of both molybdenum concentrate and primary products are compiled and published monthly and in the Minerals Yearbook by the Federal Bureau of Mines. Production figures on some primary products are not published separately because such information would reveal individual company information. Export and import data are compiled by the Bureau of Census. Information on the total quantity of molybdenum consumed in steel and quantities of molybdenum type steels produced are compiled and published by the American Iron and Steel Institute.

Data on foreign exports and imports are published in the Statistical Summary of the Mineral Industry Overseas Geological Surveys (London); Statistical Yearbook of the United Nations (New York); and in monthly and annual publications of the Department of Mines of the respective countries. Statistical information on the expanding molybdenum industry of Canada is published by the Mineral Resources Division, Department of Mines and Technical Surveys, Ottawa.

PRODUCTION, CONSUMPTION, AND TRADE

World production of molybdenum in ores and concentrates, by countries, 1959–63, is given in table 2. World production for the period 1905–55 was published (*6*) and, for individual years, to date, in the Minerals Yearbook series.

In 1963 the United States provided 71 percent of the world's total new supply. Estimated production of the U.S.S.R. was 14 percent and that of Chile was 7 percent of the world total.

U.S. consumption of molybdenum in concentrate comprised about 54 percent of estimated world output in 1963. However, some of this was exported as molybdic oxide, ferromolybdenum, and other products for end-use consumption overseas. Reported consumption of products in the United States as shown in table 3, was about 41 percent of world concentrate output.

Molybdenum consumption data for many foreign countries are not available, but an estimate for 1963, based on supply available from stocks and new production, indicates that all other nations consumed some 26,500 tons compared with U.S. consumption of about 21,500 tons (2,500 tons of molybdenum released from the U.S. Government stockpile in June of 1962, was believed to have entered the market during 1963).

The United States is the major source of molybdenum for the free world. Exports of concentrate, molybdic oxide, and ferromolybdenum during the 1950–63 period were equivalent to about 50 percent of the U.S. consumption. Imports to the United States have been minor.

The U.S. tariff rates effective August 31, 1963, were for molybdenum ore, 24 cents per pound of contained molybdenum; for ferromolybdenum and unwrought metal, 20 cents per pound of contained molybdenum plus 6 percent ad valorem; for waste and scrap, 21 percent ad valorem; and for wrought metal 25.5 percent ad valorem.

TABLE 2.—*World production of molybdenum in ores and concentrates, by countries* [1] [2]

[Short tons]

Country [1]	1954–58 (average)	1959	1960	1961	1962	1963
Australia	1	([3])		1	1	
Austria	2					
Canada	381	375	384	386	409	500
Chile	1,457	2,532	2,042	2,019	2,628	3,352
China [4]	1,100	1,650	1,650	1,650	1,650	1,650
Japan	271	421	420	404	413	366
Korea, Republic of	19	25	49	36	82	77
Mexico	33	29	66	4	64	45
Norway	196	249	271	266	288	[4] 275
Peru	([3])				[5] 6	662
Philippines		49	31	125	125	117
Portugal	5					
South Africa, Republic of	[6] 6					
U.S.S.R. [4]	([7])	4,950	5,500	5,950	6,250	6,250
United States	27,974	25,478	34,119	33,282	25,622	32,506
Yugoslavia	4	[4] 4				
World total (estimate) [1]	35,300	35,750	44,550	44,100	37,550	45,800

[1] Molybdenum is also produced in Bulgaria, North Korea, Rumania, South-West Africa, and Spain, but production is negligible.
[2] This table incorporates some revisions. Data do not add exactly to totals shown because of rounding where estimated figures are included in the detail.
[3] Less than 500 pounds.
[4] Estimate.
[5] Exports.
[6] Average annual production 1957–58.
[7] Data not available; estimate by author of chapter included in total.

STRATEGIC CONSIDERATIONS

The United States produced more than 70 percent of the world molybdenum output in 1963 and domestic mine-mill capacity is expected to increase by about 30 percent in the next several years. Chile is a major producer, and Canada is expected soon to become a major producer. Transportation of molybdenum is not a major problem because the tonnage involved is relatively small.

TABLE 3.—*Domestic consumption of molybdenum products by end uses in 1963*

[Short tons of contained molybdenum]

End use	Molybdic oxides [1]	Ferromolybdenum [2]	Molybdenum metal powder	Ammonium molybdate	Sodium molybdate	Other [3]	Total 1963
Steel:							
High-speed	667	323				55	1,045
Hot-work tool	122	92				38	252
Other tool	123	91					214
Stainless	1,454	1,027				17	2,498
Other alloy [4]	7,948	924				65	8,937
Steel-mill rolls	871	83					954
Gray and malleable castings	220	1,417				7	1,644
Welding rods		119					119
High-temperature alloys	292	135	2			269	694
Molybdenum powder:							
Wire, rod, and sheet			411				411
Other (forging billets, etc.)	1	2	360			1	364
Chemicals:							
Inorganic pigments	259			6	12		277
Organic pigments	62			3	111	1	177
Catalysts	332			12	1		345
Miscellaneous [5]	40	343	17	12	5	392	809
Total	12,391	4,556	790	33	129	845	18,744
Stocks at consumer plants, Dec. 31	1,692	875	11	7	13	139	2,735

[1] Includes technical and purified oxides.
[2] Includes molybdenum silicide and calcium molybdate.
[3] Includes thermite molybdenum, molybdenum pellets, purified molybdenum disulfide, and molybdenite concentrate added direct to steel.
[4] Includes quantities that were believed used in producing high-speed and stainless steels because some firms failed to specify individual uses.
[5] Includes magnets, other special alloys, friction material, lubricants, pesticides, refractories, packings, etc.

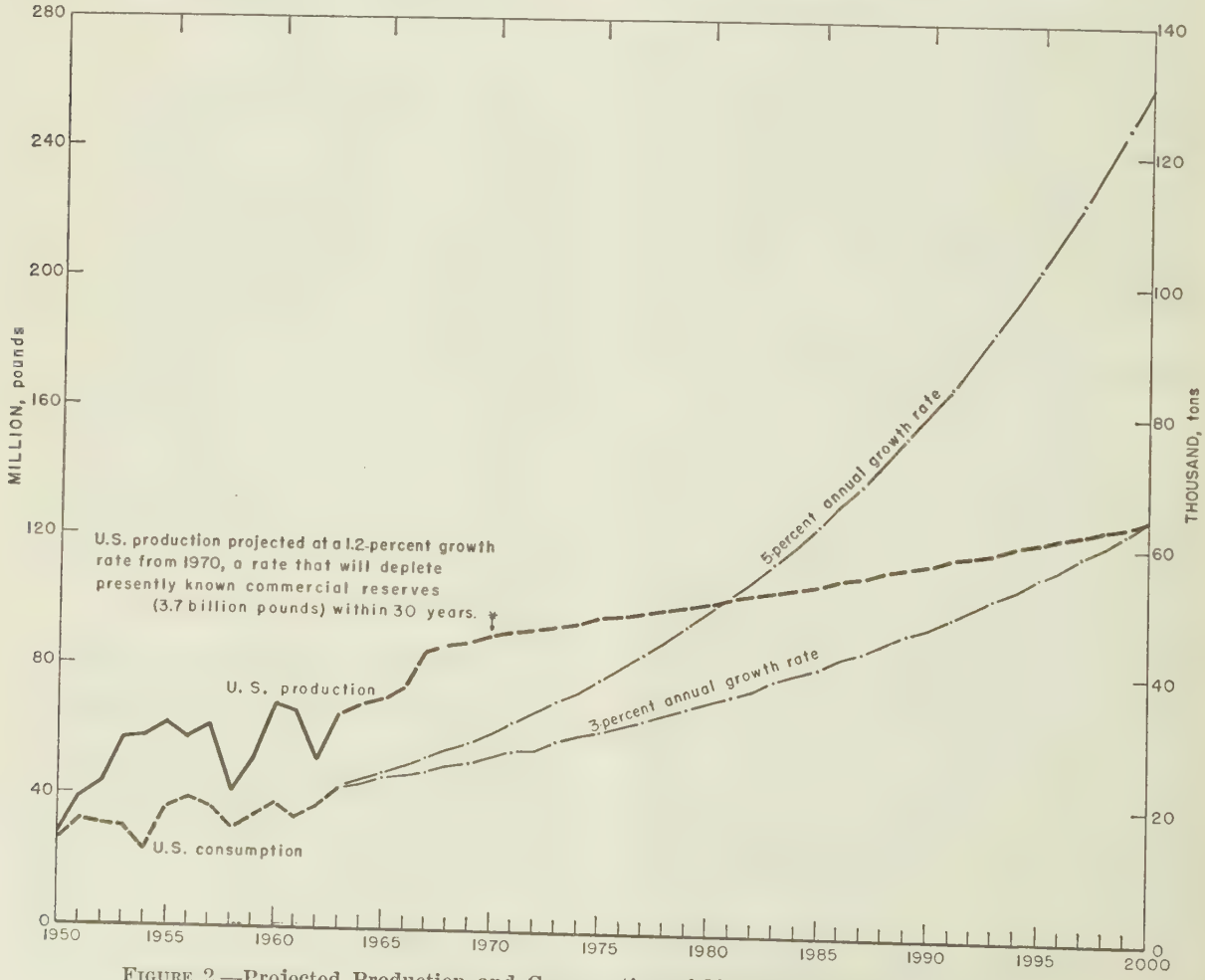

FIGURE 2.—Projected Production and Consumption of Molybdenum in the United States.

The national (strategic) stockpile contained 40,000 tons of molybdenum on June 30, 1964. Release of surplus material was expected to reduce this to 34,000 tons by the end of 1964.

Domestic ore resources, including potential ores that can be worked at sufficiently high prices, will not be depleted before the end of this century. However, a continued high rate of growth in demand will require continuing appraisal of the resource base and productive capacity.

GOVERNMENT PROGRAMS

To encourage exploration of domestic molybdenum deposits, the Office of Minerals Exploration, provides assistance to private industry, in the amount of 50 percent of the approved estimated cost, with the moneys to be repaid from production.

PRICES

The price of molybdenum has been notably stable over many years. The price of a pound of molybdenum contained in concentrate increased steadily from a low of 70 cents in 1932 to $1.40 in 1963. Price advances for ferromolybdenum, molybdic oxide, and other products paralled those for the concentrate.

TAXES

Producers are granted a depletion allowance of 15 percent on income from both domestic and foreign production.

RESEARCH

The Climax Molybdenum Co. has maintained a research department since 1924, and much of the rapid growth of the industry is attributed to its research in mining, milling, processing, and uses of the element in end products. Producers of byproduct molybdenum have increased overall recovery through improved flotation systems. Many consuming firms maintain research departments and have made significant contributions to solving processing and fabricating problems encountered and have developed new applications. Institutions have conducted research to devise means of protecting the pure molybdenum in oxidizing atmospheres at elevated temperatures and made other studies to expand knowledge of its properties and uses. The Government has sponsored much of the research on molybdenum conducted by industry and institutions, in addition to the work done by its individual agencies.

Bureau of Mines investigators have conducted mining and extractive-metallurgy research and have issued a series of reports providing thermodynamic data. Bureau research on molybdenum melting and casting procedures (2) and on the extraction of molybdenum from fused salts (4) was described in recent years.

In the last decade significant advances have been made in major problem areas: Difficulties in fabrication of arc-cast ingots have been largely overcome; quality of molybdenum sheet has been greatly improved and larger sizes are available; methods for protecting molybdenum against oxidation have markedly raised the temperature at which it can be used. Continuing research has added many new molybdenum alloys to the lists of available special property materials (7).

The Climax Molybdenum Co. and Battelle Memorial Institute have published data on the properties and uses of molybdenum and its alloys.

OUTLOOK

Inasmuch as the domestic steel industry accounts for about 80 percent of the U.S. molybdenum consumption, future trends in steel production will largely determine the future consumption of molybdenum. Two factors suggest that total domestic and export demand for molybdenum will increase at a faster rate than domestic steel production. One, alloy steel comprises an increasing proportion of total steel and molybdenum use per ton of steel is increasing. Two, foreign steel production, increased by 280 percent between 1950 and 1963. The consumption of metallic molybdenum, molybdenum-base alloys, and molybdenum compounds is also increasing but as the growth rate relates only to about 20 percent of total consumption it will not significantly influence the overall growth rate. However, a closer relationship has been shown in the postwar years between molybdenum consumption and real gross national product (RGNP). Domestic molybdenum consumption has averaged a 5-percent growth rate while RGNP has averaged slightly more than 3.5 percent. If this relationship holds, and a RGNP growth rate of about 3.75 percent is anticipated, future growth in molybdenum consumption can be expected to increase at least by 3 percent and probably by

5 percent annually as long as it is readily available at a real price only slightly higher than in 1964.

As shown in figure 2, domestic molybdenum production is expected to reach 45,000 tons by 1970, and will equal the projected consumption of 30,000 tons plus exports of 15,000 tons. However, in subsequent years, production in excess of 45,000 tons will be increasingly costly. Thus, although production will increase in response to demand there may be some slowing of the demand-growth rate because of tightened supply or higher price.

Increased production costs per unit of molybdenum will not be due to depletion of the overall reserve but primarily will be due to the difficulty of expanding productive capacity. Recovery of byproduct molybdenum which is relatively low in cost, will comprise a smaller proportion of total output, and mines which produce molybdenum as a principal product may have inherent limitations, as to size, for economic operation. Therefore, new plant, and development of less economic deposits, will be necessary.

During the 14 years (1950–63) U.S. exports of molybdenum were equivalent to about 50 percent of domestic consumption. On this basis, 15,000 tons of molybdenum will be available from the United States in 1970 plus 10,000 to 15,000 from other free world sources and possibly 10,000 tons from China and the U.S.S.R., for a total supply of 35,000 to 40,000 tons for foreign consumers.

Assuming a 3 to 1 ratio of foreign steel production to U.S. steel production, as in 1963, foreign demand for molybdenum in 1970 might approach a 3 to 1 ratio with U.S. consumption, or 80,000 to 90,000 tons. Therefore, although estimates of the future balance between foreign demand and supply are tenuous, there is reason to believe that any lag in the growth rate for domestic demand, below 5 percent, probably will be compensated by the export market.

PROBLEMS

The overall problem of maintaining balance between domestic supply and demand will not be critical in this decade and probably not before 1980. However, component parts of the problem need immediate and continuing study.

The need for more flexibility in production rates, to meet fluctuation in demand, was manifest in the shortages of 1962, 1963, and 1964. The question of equity between domestic and export demand, also evident in these shortages, involves political, economic, and national defense considerations.

Prudent use of molybdenum resources will be increasingly important in future years to assure a continuing supply of molybdenum for essential applications. For example, some molybdenum alloy, catalyst, or other molybdenum-bearing material might continue in use where a more plentiful substitute would perform as well. Another need is for economic methods of reclaiming molybdenum-bearing scrap now being lost by dilution in products where this metal is not needed.

Industrial, defense, and space programs have brought molybdenum applications technology to an advanced stage, but continued research to improve high-temperature strength, fabricability, oxidation resistance, and other properties are needed.

Extractive technology also is well advanced but research is needed for expansion of the resource base. Lower cost sampling, mining, and concentrating procedures are needed to permit exploitation of small or inaccessible deposits which currently cannot support plant amortization. Improved recovery from copper, uranium, tungsten, and other ores and economic extraction from vanadiferous shales are appropriate subjects for additional study.

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NICKEL

By Glen C. Ware [1]

NICKEL is used in world production of ferroalloys in an amount exceeded only by chromium. When alloyed with other metals it imparts strength, toughness, hardness, and ductility together with resistance to oxidation and corrosion. Nickel is a component of a series of magnetic alloys and alloys for use in resistance heating elements. Metals are clad with nickel to protect them from corrosion and coated with it to gain luster and beauty.

Although nickel deposits are found worldwide, 90 percent of free-world supply is produced by 3 Canadian companies and a company in New Caledonia. The United States consumes about half of free-world production. Domestic production is derived from Nickel Mountain, an ore deposit near Riddle, Oreg. The ore, containing about 1.5 percent nickel, is expected to support the present production rate through the year 1978.

Canadian nickel is derived chiefly from pentlandite, a sulfide mineral associated with pyrrhotite and chalcopyrite. In the Sudbury area, as many as 14 products are obtained, chief of which are nickel, iron ore, copper, and the platinum-group metals. A new deposit opened at Thompson, Manitoba, contains less of precious metals, but a modern, highly efficient plant and an abundant reserve assure profitable operation and ability to expand to meet foreseeable demands for nickel. Garnierite is exploited in the only United States nickel plant. Although the output is small compared with U.S. demand for nickel, the operation is important as a possibility to expand domestic production if ample reserves should become available through discovery or improved benefication methods.

Laterite and serpentine deposits are widespread throughout the tropics and constitute the world's largest source of nickel. They are being exploited in Cuba, New Caledonia and the Celebes and being investigated in the Dominican Republic, Central America, New Guinea, and the Philippines. The difference in composition of the various nickel ores requires a variety of mineral dressing methods, and complex pyrometallurgical, chemical and electrolytic processes are needed to recover nickel.

During the period 1959–63 more than 80 percent of the primary nickel consumed in the United States went into the manufacture of alloys. The largest single application was to the manufacture of stainless steels where the use is expected to increase significantly.

During 1959–63 the consumption of nickel averaged 116,500 tons per year, an increase of 9 percent over that of 1954–58. Owing to newly developed uses, increased use in new product lines, and the availability of nickel, consumption is expected to rise sharply throughout the world.

One of the more important remaining metallurgical problems is that of achieving high recovery of nickel from laterite and serpentine ores. Other problems involve the efficient and economic separation and recovery of coproduct or byproduct metals from ores, scrap alloys, and spent catalysts. Among the many physical metallurgical problems in the development and utilization of new alloys are those connected with the preparation of extremely pure nickel and of high-strength, high-temperature alloys to withstand extreme temperature changes.

BACKGROUND

Coins of Asia Minor of the pre-Christian era contained nickel, and its alloys are mentioned in ancient Persian fables in which the mythological warriors fashioned their "Heaven-sent" blades from meteoric iron. By the ninth century A.D. the Chinese used a nickel, copper, and zinc alloy called paitung or "white-copper." Nickel began its Western history in Saxony, Germany, in the middle of the 18th century

[1] Commodity specialist.

when miners stumbled upon it while working with lodes of copper and silver ore. Smelting of this ore produced a hard white shiny metal, seemingly full of promise, but not being able to work the metal into useful articles, the superstitious miners named the ore "kupfernickel" after "Old Nick" and his mischievious gnomes whose duties were to plague the workers and bewitch the raw materials.

In 1694 W. Hiarne described kupfernickel as having the appearance of copper ore but yielding no copper. The Swedish scientist Axel Cronstedt identified nickel as an element, isolating it from a copper-nickel ore. Twenty-five years later Bergmann confirmed the discovery. In 1776 G. von Engestrom showed that paitung contained nickel, copper, and zinc. In 1781 Richter produced the first nickel pure enough to enable him to describe its physical and chemical properties with remarkable accuracy.

The use of nickel was limited largely to making German-silver alloys until Faraday developed electroplating. By 1844 plating was firmly established in England. A further impetus to greater use of nickel resulted from a change in policy toward token-money coinage. In 1860 Belgium adopted a composition of 75 percent copper and 25 percent nickel for some of its coins. The United States did the same in 1865, Germany in 1873, and Switzerland in 1879. Joseph Wharton's work with a malleable pure nickel enabled Switzerland to issue pure nickel coins 2 years later. At the same time Fleitmann pioneered in the development of nickel-clad steel.

Until 1870 nickel production was limited to small deposits in China, Germany, Greece, Italy, Norway, Sweden, and the United States. From 1853 to 1893 only about 2,000 tons of nickel was produced domestically at the Gap mine near Lancaster, Pa., and at Mine La Motte near Fredericktown, Mo.

In 1864, nickel silicate ore was discovered in New Caledonia by Garnier, after whom the mineral, garnierite, was named. Commercial mining in New Caledonia, began in 1874 and New Caledonia was the principal source of nickel until 1905 when Canada became the leading producer. The mine at Riddle, Oreg., was brought into operation in 1954.

The International Nickel Co. of Canada, Ltd. (Inco), the world's largest nickel producer, was formed in 1902 by a merger of the Canadian Copper Co. and the Orford Copper Co.

The free world capacity to produce nickel is estimated at more than 330,000 tons annually, Canada alone accounting for more than 250,000 tons. Inco has a rated annual capacity of 200,000 tons; Falconbridge Nickel Mines, Ltd., 37,500 tons; and Sherritt Gordon Mines, Ltd., 15,000 tons. The annual rated capacity of the Cuban plants seized by the present Cuban government is 50,000 tons, but production is reported to be about half this rate. The U.S.S.R. is estimated to produce about 100,000 tons of nickel per year.

Large scale smelting and refining of nickel ores became feasible when the Orford process to separate nickel and copper mattes was combined with the Mond process to refine nickel. By the Orford process sodium sulfide is heated with the matte to produce a melt from which a layer of copper-sodium sulfide separates and floats on a layer of nickel sulfide. After the melt has cooled the solid layers are separated with a blow of a hammer. In the Mond process the nickel sulfide is roasted to oxide which is reduced to pure nickel with hydrogen and carbon monoxide. A volatile nickel carbonyl is produced which can be decomposed by heat to produce nickel and regenerate carbon monoxide. Both of these processes, were reduced to practice in the last decade of the 19th century, and their application brought Canada into first position as a producer of nickel in 1905. Modern mineral dressing technology has replaced this method making it only of historic interest.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

In 1963, the United States consumed 48 percent of the nickel produced in the free world, and contributed only 4 percent of world production. The Hanna Nickel Smelting Co., Riddle, Oreg., produced 10,700 short tons and 700 tons was a byproduct of copper. The Hanna company markets ferronickel recovered from ore mined by the Hanna Mining Co. The smelter has a capacity of about 14,000 tons per year. National Lead Co., Fredericktown, Mo., had recovered nickel from complex ore but the mine and refinery were closed in 1961.

Many companies, the largest ones at Cleveland and Cincinnati, Ohio, produce 3,000 to 3,500 tons of nickel salts annually using metal, residues, oxide, and scrap. Table 1 lists United States refiners and processors and their products.

The principal nickel producing countries in the free world during 1959–63 were Canada with 77 percent of the total free world production; New Caledonia, 13 percent; United States, 8 percent; and Republic of South Africa and Finland, 1 percent each. The total capacity of free world mines is estimated to be about 330,000 tons of nickel per year. Of this total, the capacity of Canadian producers amounts to about

250,000 tons. Table 2 gives estimates of nickel producing capacity of various firms and countries at yearend 1963. The expropriated U.S. Government facilities at Nicaro and those of the Freeport Sulphur Co. at Moa Bay, Oriente Province, Cuba are reported to be producing nickel at an annual rate of about 50 percent of their original combined capacity of about 50,000 tons of nickel.

TABLE 1.—*Refiners or processors of nickel in the United States in 1963*

Refiner or processor	Location of plant	Nickel products made
Allied Chemical Corp., General Chemical Division.	Marcus Hook, Pa.	Carbonate, salts.
American Metal Climax, Inc.	Carteret, N.J.	Sulfate.
American Smelting and Refining Co.	Perth Amboy, N.J.	Do.
Baker Chemical Co., J. T.	Phillipsburg, N.J.	Carbonate, salts.
Hall Chemical Co.	Wickcliffe, Ohio	Carbonate.
Hanna Nickel Smelting Co.	Riddle, Oreg.	Ferronickel.
Harshaw Chemical Co.	Cleveland, Ohio	Carbonate, salts.
International Nickel Co. of Canada, Ltd.	Huntington, W. Va.	Alloys, metal.
McGean Chemical Co.	Cleveland, Ohio	Carbonate, salts.
Nuodex Products Co., Inc.	Elizabeth, N.J.	Salts.
Phelps Dodge Refining Corp.	Laurel Hill, N.Y.	Sulfate.
Do.	El Paso, Tex.	Do.
Shepherd Chemical Co.	Cincinnati, Ohio	Carbonate, hydrate, salts.

TABLE 2.—*Size and distribution of principal producers of nickel*

Country and producer	Location of mines	Refined nickel products (short tons of nickel)	
		Annual capacity end of 1963	Planned annual capacity by 1963
Canada:			
The International Nickel Co. of Canada, Ltd.	Sudbury, Thompson.	205,000	225,000
Falconbridge Nickel Mines, Ltd.	Sudbury	38,000	45,000
Sherritt Gordon Mines, Ltd. (refinery capacity).	Lynn Lake, Fort Saskatchewan.	15,000	15,000
New Caledonia: Société le Nickel.	New Caledonia	32,000	39,000
Japan: Refinery capacity (using imported ores).		25,000	30,000
United States: The Hanna Mining Co.	Riddle, Oreg.	13,000	14,000
Byproduct production from copper refining.		700	850
Other countries: Brazil, Finland, Morocco, Southern Rhodesia, and Republic of South Africa.		600	1,000

Supply of nickel to the United States comes chiefly from Canada, which supplied approximately 90 percent of the total U.S. nickel imports in the period 1959–63. Most of the nickel imports were supplied by Inco. Other Canadian suppliers were Falconbridge Nickel Mines, Ltd., and Sherritt Gordon Mines, Ltd. The supplier of New Caledonian nickel was Société Le Nickel, S.A.

The International Nickel Co. of Canada, Ltd., operates Creighton, Frood-Stobie, Garson, Levack, Murray and Clarabelle mines in the Sudbury district, Ontario, and the huge Thompson mine at Thompson, Manitoba. The firm also operates ore concentrators at Copper Cliff and Creighton, smelters at Copper Cliff and Coniston, and a refinery at Port Colborne, in the Sudbury district. It also operates a nickel refinery at Clydach, Wales, and a large rolling mill at Huntington, W. Va. It recently established a new research laboratory at Sterling Forest, N.Y. Inco's nickel plant at Thompson is a fully integrated complex. Activities at this recent development range from mining to production of nickel metal in various forms. Annual nickel-producing capacity at the Thompson complex has been expanded from the planned 38,000 tons to over 45,000 tons.

Falconbridge Nickel Mines, Ltd., operates the Falconbridge, East, Hardy, and Fecunis mines in the Sudbury district, a smelter at Falconbridge, Ontario, and a refinery at Kristiansand, Norway. In 1963, Falconbridge's total mine development advances amounted to 42,000 feet, and total diamond drilling totaled 344,000 feet. Drilling and other mine development programs were initiated by the Marbridge Mines Ltd., a firm jointly owned by Falconbridge and Marchant Mining Co., Ltd.

Sherritt Gordon Mines Ltd., operates mines at Lynn Lake, Manitoba, and a refinery at Fort Saskatchewan, Alberta. Other Canadian producers of nickel materials are Giant Mascot Mines, Ltd., Metal Mines Ltd., Raglan Nickel Mines Ltd., and McIntyre Porcupine Mines Ltd.

The largest nickel ore mining operation in New Caledonia is on the Thio Plateau. The refinery center is at Pointe Doniambo where nickel-sulfide matte and ferronickel are produced. The matte is shipped to Le Nickel's refinery at Le Havre, France, for conversion to refined nickel.

GRADES AND SPECIFICATIONS

Primary nickel products of smelters and refineries are chiefly metal, oxide, and ferronickel. Most primary nickel metal in the United States is sold as electrolytic cathodes, whole or cut into convenient sizes, containing 99.95 percent nickel. Nickel metal also is supplied in ingots, shot, briquets, pellets, and powder. National stockpile specifications for various forms of metal and oxide are given in table 3.

TABLE 3.—*Nickel purchase specifications for national stockpile* [1]

Constituent	Chemical requirements, weight-percent					
	Metal				Oxide	
	Electrolytic	Ingots	Briquets	Shot	Powder	Sinter
Nickel plus cobalt, minimum	99.50	98.50	99.50	98.90	76.50	[2]76.50
Cobalt maximum	1.00	1.00	1.00	1.00	1.00	1.10
Iron maximum	.25	.90	.25	.60	.50	3.00
Sulfur maximum	.02	.07	.02	.05	.05	.08
Carbon maximum	.10	.30	.10	.25	.10	.10
Copper maximum					.30	.30

[1] National Stockpile Specification P–36–R, Oct. 11, 1956.
[2] When the nickel plus cobalt content of sintered nickel oxide exceeds the minimum requirement the cobalt, iron, sulfur, carbon, and copper may increase proportionately.

NOTE. Physical requirements follow:
1. Electrolytic nickel shall be in the form of rectangular cathodes, cut or uncut, of any thickness or dimensions usual with the producer, except that all cathodes in a lot shall be of the same dimensions, which shall be not less than 4 by 4 inches nor more than 27 by 36 inches.
2. Nickel ingots and nickel briquets may be of any size and shape usual with the producer, but all ingots or briquets in a lot shall be of the same size and shape. Material shall have a clean surface, free from dirt, slag, or other foreign materials.
3. Nickel shot may be of any size usual with the original producer.
4. No particle size requirements shall apply to nickel oxide.
5. All sintered nickel oxide shall pass a 2-inch sieve. Not more than 10 percent by weight shall pass a ¼ inch U.S. Standard Sieve (A.S.T.M. Designation E 11). Sintered nickel oxide shall contain not less than 99 percent by weight of sintered material.

Source: General Services Administration, Defense Materials Service.

Ferronickel is an alloy of iron and nickel. Domestic ferronickel is cast into 50-pound pigs and contains 40 to 50 percent nickel, 49 to 59 percent iron, 0.5 percent cobalt, 0.10 percent chromium, 0.050 percent phosphorus, 0.015 percent carbon, 0.010 percent sulfur, and 0.30 percent copper. The compositions of some nickel alloys used by industry are given in table 4.

TABLE 4.—*Composition of commercial forms of nickel used by industry, in percent*

Constituent	"F" nickel shot and ingots	Nickel-copper-chromium-iron pigs	Nickel-chromium-iron pigs	Nickel-silicon granules
Nickel (including cobalt)	92.00	57.00	46.00	59.00
Chromium		8.00	16.00	
Copper	.20	23.50	.25	
Manganese		.50	.40	
Silicon	5.50	1.25	.45	29.00
Carbon	.55	1.25	1.70	
Sulfur	.06			
Iron	1.65	[1] Balance	[1] Balance	[2] Balance

[1] Iron and impurities.
[2] Iron and other inclusions.

Cobalt content of 2 to 3 percent in engineering alloys imparts harmful effects if used for atomic energy applications, where the maximum tolerable amount is 0.2 percent. Cobalt content up to 7 percent imparts no seriously harmful qualities to nickel anodes. However, for fabricating engine valves, where cobalt interferes with the normal heat treatment cycle, 1 percent is the maximum that can be tolerated.

The National Bureau of Standards (NBS) has available three nickel oxide standard samples designated with the following numbers: NBS 671, NBS 672, and NBS 673. These standards are intended for use in checking and calibrating chemical and spectrochemical methods used in the analysis of high-purity nickel, particularly electronic-grade and electrolytic nickel. Four new high-temperature alloy standards designated as, Udimet 500, Inco 713–A, Inco 713–B, and Inco 713–C are available from the NBS. These samples are intended for use in optical emission and X-ray fluorescent analysis. Nickel content of these alloys ranges from 51.9 percent for Udimet 500 to 75.5 percent for Inco 713–A.

TECHNOLOGY

Geology

The nickel deposits fall into three general classifications—nickel-copper sulfides, nickel silicates, and nickel laterites and serpentines. Most of the nickel produced at present is from the huge Canadian deposits of the sulfides of nickel, copper, and iron, chiefly pentlandite $(NiFe)_9S_8$, chalcopyrite $CuFeS_2$, and pyrrhotite Fe_7S_8. These ores occur in large disseminated bodies and in small-to-moderate-size massive sulfide bodies. In addition to nickel, copper, and iron, ores contain varying quantities of cobalt, gold, silver, selenium, tellurium, and platinum-group metals.

The largest known deposits of nickel silicate ores, mostly garnierite, are in New Caledonia. Garnierite is a green hydrous nickel-magnesium silicate of variable composition $(H_2(NiMg)SiO_4 \cdot nH_2O)$. The intensity of its green color is directly proportional to the nickel content. In addition to the New Caledonian deposit, there are commercially significant nickel silicate deposits in South America, Indonesia, and the United States.

Nickeliferous laterite mantles are formed by weathering of ultrabasic rocks, notably serpentine. The content of weathered minerals decreases with depth down to unweathered rock without demarcation, and the deposits are referred to as laterite and serpentine. The typical composition of these mantles is about 40 percent iron, 1 percent nickel, 2 percent chromium oxide, and 0.05 percent cobalt. Laterite type deposits constitute the largest known potential resource of nickel in the world. Nickeliferous iron laterite deposits, measured in hundreds of millions of tons, occur in Cuba, the Philippine Islands, the Celebes Islands, and parts of Borneo. Smaller and lower grade deposits are found in Japan, Madagascar, U.S.S.R., Greece, Puerto Rico, and elsewhere.

Small quantities of native alloys of nickel and iron of terrestrial origin, have been found in New Zealand, Greenland, Oregon, and British Columbia. Similar alloys are also common constituents of meteorites.

Mining

Virtually all Canadian sulfide nickel ore is mined by conventional underground methods. Cemented sand fill is gaining wider application because it results in increased recovery of ore with less dilution. Silicate ores such as garnierite and laterite usually are mined from open-pits with power shovels and trucks as in Cuba and New Caledonia. However, at the Hanna open-pit operation, near Riddle, Oreg., broken ore is trammed down Nickel Mountain and generates power in the electric generators used to brake the tram in its descent from the mine 2,000 feet above the smelter.

The Hanna Mining Co. mines garnierite and several associated minerals which occur in altered peridotite. Ore containing an average of 1.2 percent nickel is dug largely without blasting from 40-foot minimum-width benches spaced at 20-foot vertical intervals. Thirty-ton trucks are loaded with 2½ to 3½-cubic-yard shovels. Boulders of residual rock are rejected. The ore is screened at the mine, and the minus-5-inch material is sent to the tramway surge pile. The oversize is crushed and visually classified into reject and ore. Efforts to blend the ore into a uniform feed to the melting furnaces begin at the mine and persist through all the subsequent operations.

At Canadian mines, where ore formation favors bulk mining, the "blast-hole" and "caving" methods are used. These procedures are more economical than earlier types of shrinkage mining. The blast-hole method has two advantages over shrinkage stoping: More economical distribution of powder and extension of diamond-drill holes to 40 to 100-foot depths. In early shrinkage stoping the holes were seldom drilled beyond 9 feet for each blast. Subsequently, when the powder is detonated at these lower depths, all the ore is torn from the ore face. The resulting large empty space, in turn, allows greater clearance for the broken ore to fall freely to the boxholes. More importantly, the blast-hole method provides safer working conditions for the miners. Since they are not exposed to openstope backs as in shrinkage stoping, they do their drilling in small, safe drift openings.

In the caving method the ore is completely undercut on the bottom of the stope area, and the vertical sides of the stope block are so weakened that the mass of ore gradually collapses of its own weight. When the characteristics of the ore body are right for caving the moving mass of ore is crushed and broken as it caves. The crushed ore is removed through draw holes under the caving block.

Mining practices for silicate and lateritic ores are simple since these deposits are relatively shallow, regularly formed layers covered with a thin, moderate overburden. These ores usually are soft and claylike and are excavated by bulldozers, shovels, and draglines. The first step is the stripping of the overburden, and the second is the collection of ore by power shovel or dragline and loading it into conveyors.

Metallurgy

Nickel is derived from two general types of ore, silicate and sulfide, requiring different extractive methods. Generally, silicate ores cannot be beneficiated by mineral dressing techniques, but sulfide minerals are readily floated or separated magnetically from matrix rock.

Typically an ore from the Sudbury district of Canada is crushed and a nickel concentrate is separated magnetically. The remaining crushed ore is ground and an iron concentrate is separated magnetically and pelletized for blast furnace smelting. The remaining sulfides of copper and nickel are separated by flotation.

The nickel flotation concentrate is treated by an ingenious method. It is roasted with a flux and melted into a matte, which, when cooled slowly, solidifies into a mass containing three separate phases; nearly pure nickel sulfide, copper sulfide, and a nickel-copper alloy containing most of the precious metal content of the ore. The mass is ground; the alloy is recovered magnetically and refined by electrolysis to recover nickel and a residue

containing the precious metals. The nickel and copper sulfides are separated by flotation. Copper sulfide is bessemerized to blister copper and refined by electrolysis. In older plants some nickel sulfide was sintered for sale as oxide; some was roasted for subsequent refining by the Mond process; and some was reduction roasted and cast into anodes. In newer plants the matte is cast directly into anodes for electrolytic refining in which cobalt oxide, elemental sulfur, and a precious metal concentrate also are recovered. The economy attending the use of nickel sulfide anodes in refining favors an increase in the proportion of cathode nickel in the market products. This trend is being hastened by the adoption by electroplaters of anodes consisting of titanium baskets filled with chopped cathodes, eliminating the cost of casting special nickel anodes.

Cuban plants use chemical extraction to recover nickel. The plant at Nicaro leaches with ammonium carbonate and ammonia and recovers basic ammonium carbonate. At Moa Bay sulfuric acid is used to extract the nickel and cobalt which are precipitated with hydrogen.

New Caledonia was the leading producer of nickel prior to the rise of the Canadian industry. In the early plants a nickeliferous silicate of iron and magnesia was smelted with gypsum to produce a matte which was refined to ferronickel in converters. Modern electric furnaces are now used to smelt the ore with coke breeze, producing a refined ferronickel suitable as a master alloy in making special steels.

The Hanna Nickel Smelting Co. smelts garnierite ore at Riddle, Oreg., by the d'Ugine process. The ore is melted in electric furnaces and poured into reaction ladles where reduction is accomplished by adding crushed ferrosilicon to the stream of molten ferronickel. Alloy containing more than 50 percent nickel is made for export, but the average is held to 48 percent to minimize loss of metal in the slag.

At the Sherritt Gordon Mines, Ltd., Fort Saskatchewan, Alberta, sulfide ore is leached with ammonia and oxygen. Copper is separated from the leach liquor with hydrogen sulfide. The liquor is further treated to separate nickel and cobalt which are reduced with hydrogen and recovered as powder. Silicate ores are amenable to this process if first given a sulfating roast. The powdered nickel and cobalt are ideal chemical starting materials and command premium prices. The company has developed a strip rolling process in which powder is compressed into strip, sintered and rolled into fully dense strip suitable for coin blanks or for fabrication into other useful forms.

USES

Nickel has hundreds of important, varied uses. Based on a 1959–63 average annual consumption of 117,000 tons, the largest users were ferrous alloys, 47 percent of the total; nonferrous alloys, 23 percent; electroplating, 15 percent; high-temperature and electrical-resistance alloys, 10 percent; and other uses, 5 percent. Stainless steel accounts for the largest single use of nickel, taking 32,000 tons annually during 1959–63 for the austenitic chromium-nickel types containing 6 to 22 percent nickel.

The austenitic stainless steels of the 300 series are the most important of the nickel-bearing stainless steels. Type 302 with 8 to 10 percent nickel and 17 to 19 percent chromium is a general purpose alloy with many applications. Type 301, an alloy with a lower nickel content than type 302, is used for structural members in aircraft, trucks, and railroad cars where high strength is required. For use at elevated temperatures nickel content of the alloys is increased to 10 to 22 percent and that of chromium, 24 to 26 percent. Higher amounts of nickel and chromium impart to the alloys superior resistance to high-temperature corrosion and scaling in addition to higher strengths.

The automotive industry is the largest single consumer of stainless steels. The largest tonnage goes into decorative trim and other ornamental applications, replacing chromium stainless which does not withstand the corrosive conditions in cities where salt or calcium chloride is used for snow removal or the air contains corrosive industrial gases. Stainless steel is used for structural purposes in trucks, buses, and trailers, but not in passenger cars.

The second largest use of nickel, taking an annual average of 27,000 tons during 1959–63, was for nonferrous alloys. These include nickel-copper, copper-nickel, nickel-chromium, nickel-molybdenum alloys, and superalloys. The most important alloys in the nickel-copper category are the various types of Monel metal. The basic Monel metal which contains about 66 percent nickel and about 32 percent copper, is strong, tough, ductile, and corrosion resistant. Its resistance to corrosion by foods and household cleaning solutions has led to widespread use in dairy and food manufacturing industries. The alloy retains its bright silvery luster in clean outdoor atmospheres; in polluted atmospheres it tarnishes but does not corrode. It is used for roofing and other architectural applications.

The most important nickel-chromium alloys known as Inconels and Illiums have typical compositions of 73.0 percent Ni, 15.0 percent Cr;

and 64.0 percent Ni, 22.0 percent Cr, respectively. The chromium gives these alloys more resistance to corrosion under powerful oxidizing conditions, and the high nickel content gives resistance to corrosion under reducing conditions. The first of the Inconel series had a composition of 76.0 percent Ni, 15.8 Cr, and 7.20 Fe. It was first used in the dairy industry and has since become widely used for such applications as furnace muffles, chemical and food processing equipment, gas turbines, and jet and rocket engines. Because recently developed Inconel alloys can withstand extremely high temperatures, the skin of the X–15 rocket research plane was made from Inconel alloy X–750. The Illium alloys resist corrosion by sulfuric and nitric acids over a wide range of concentrations and temperatures. The alloys are used in pumps, valves, tubing, and other equipment subject to severe acid corrosion.

Nickel-molybdenum and nickel-molybdenum-chromium alloys known as Hastelloys, were developed to resist corrosion by hydrochloric acid and later modified in composition to provide superior corrosion resistance to other mineral and organic acids. They are used primarily for industrial pumps, vats, distillation columns, and other industrial equipment for handling acids and alkaline bleaching solutions. Alloy C with a composition of 55 Ni, 17 Cr, and 17 Mo is one of the few alloys which will resist attack by wet chlorine gas and chlorine dioxide solutions.

The term superalloy was used after World War II to describe a family of high-temperature, high-strength alloys, nearly all containing nickel, and many nickel-based. When aluminum and titanium are added to the above alloys, compounds such as Ni_3Al and Ni_3Ti are formed which greatly strengthen the alloys by precipitation hardening. Most of these superalloys are used below 2,000° F.

An important step in extending the use of superalloys above 2,000°F. was made in 1962 by the E. I. du Pont de Nemours & Co., Inc. with the development of TD-Nickel, an alloy containing 98 parts nickel and 2 parts thoria. The thoria is dispersed uniformly in submicron-size particles. TD-Nickel is much stronger than standard superalloys above 2,000° F., tests showing an ultimate tensile strength of 10,000 pounds per square inch at 2,400° F., at which standard superalloys are virtually useless.

Electroplating accounted for 17,000 tons per year of the nickel used during 1959–63. However, since 1946 minor amounts of nickel have been used to plate various basic materials by techniques which do not require an impressed electric current. Among these methods are the Niphos process, immersion and electroless plating, and the vacuum or sputtering plating.

Nickel is used in electroforming in which a negative matrix is heavily coated with electrodeposited metal to produce useful objects such as fountain pen caps. Phonograph record master dies are electroformed on positive matrices so that they will reproduce positive copies, and they may be backed for strength and plated with chromium to harden the working surface. Highly detailed features can be produced precisely without the need of expensive tooling.

Nickel cast irons consumed an average of 5,000 tons of nickel per year during 1959–63. Nickel in cast iron improves its machinability and resistance to creep, and it imparts uniformity to the hardness of castings. The addition of chromium or molybdenum or both greatly improves the strength of nickel cast irons and their resistance to wear and corrosion. Major uses for nickel cast irons are cylinder blocks, cylinder liners and pistons, industrial melting pots, molds, and steel mill rollers.

Other uses of nickel include catalysts, magnets, and batteries. During 1959–63 an annual average of 1,600 and 850 tons of nickel was used for catalysts and magnets, respectively. The precise amount used for batteries is not known. The most important catalytic use of nickel is for hydrogenation of fats and oils. Nickel is an important constituent of the Alnico type of permanent magnets, used principally in loudspeakers. With the advent of cordless electrical appliances demand for nickel-cadmium batteries has grown. Nickel is used in the ceramic industry for preparing iron sheets prior to enameling and also in the preparation of carbides and other hardfacing materials, glass, lubricants, fuel additives, plastics, rubber, salts, and fungicides.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

A comparatively small quantity of nickel is obtained as a byproduct from cobalt ore, silver-cobalt ores, copper ores, platinum ores, and copper-lead ores. Usually, however, nickel is the chief value in the ores in which it is found associated with other metals and elements. The sulfide ores of the Sudbury district, Ontario, also contain copper, gold, silver, cobalt, tellurium, iron, and plantinum-group metals which are recovered as byproducts or coproducts of nickel processing. The nickel sulfide ores of the Lynn Lake region, Manitoba, contain mostly copper and cobalt, which are also recovered. The nickel silicate ores of Riddle, Oreg., contain minute quantities of cobalt, which are not recovered as a separate product.

Complete realization of the values in the ore is an important factor in the development of mining and metallurgy in the Sudbury area where the smelters and refiners recover as many as fourteen elemental products; they deliver sulfur dioxide to chemical plants to be liquefied or converted into sulfuric acid; and they return waste to the mine for fill. Inco produces iron ore, nickel, copper, cobalt, selenium, tellurium, sulfur, gold, silver, platinum, palladium, rhodium, ruthenium, and iridium.

ALTERNATE MATERIALS

High nickel alloys can be replaced substantially by nickel-chromium-molybdenum steels, boron-bearing steels, chromium-manganese-nickel stainless steels, and nickel-free stainless steels. Should the price of nickel rise significantly, considerable saving might be made by replacing high-nickel steels with case-hardened steel, lower nickel-content stainless steels and nonferrous alloys of lower nickel content. More extended use could be made of iron base alloys and iron-chromium-aluminum alloys in electrical resistors.

A copper alloy with 10 percent nickel and aluminum-base alloys can be substituted for cupronickel alloys for condenser tubes. Nickel can be conserved by replacing Alnico magnets, which contain 14 to 28 percent nickel, with magnets made of iron powder, bismuth-manganese, or barium-ferrite. It may be further conserved by reducing the amount of nickel in aluminum-base and other metal-base alloys. Nickel-plated and nickel-clad products can be used where only surface protection is needed.

SECONDARY SOURCES AND RECOVERY

The largest source of secondary nickel is stainless steel scrap, particularly the 300 series which contain 7 to 36 percent nickel. The second largest source is nonferrous alloy scrap such as cupronickel, nickel-silver alloys, and other nickel alloys. Spent catalysts and high-temperature alloys are important. Table 5 gives the consumption of new and old nickel by users and by the form in which it is used.

Nickel in scrap alloys is most effectively reused by including the scrap in the composition of more alloy, stainless steel going into stainless steel alloys, and other scrap into counterpart alloys. Other forms of nickel recovered from nonferrous scrap are metal, nickel-base and copper-base alloys, ferrous and high-temperature alloys, and various chemical compounds.

Very little of the nickel consumed in electroplating is recoverable as scrap except for small quantities in electrode sludge and spent plating solutions. Spent catalysts also are a small source of secondary nickel.

Insufficient data are available on the disposition of high-temperature alloy scrap. On account of various economic and technological reasons, only a relatively small quantity is treated for recovery of the more expensive constituents. In recent years large quantities of this type of scrap have been exported to Japan, West Germany, and other countries where either the scrap or its constituents are reclaimed. Table 6 gives the quantity of nickel recovered in the United States by type of scrap and by the form recovered.

TABLE 5.—*Consumption of new and old nickel, nickel-base, and nickel silver scrap in the United States*

[Gross weight, short tons]

	1962		1963	
	New	Old	New	Old
Smelters and refiners:				
Unalloyed nickel	704	260	753	294
Monel metal	483	1,166	505	979
Nickel silver [1]	345	3,559	313	3,377
Miscellaneous nickel alloys	2	4,130	7	4,525
Nickel residues	4	27	-------	9
Total (nickel-base)[1]	1,193	5,583	1,265	5,807
Foundries and other plants:				
Unalloyed nickel	1,418	1,610	1,637	668
Monel metal	214	548	123	495
Nickel silver [1]	8,518	47	8,133	55
Miscellaneous nickel alloys	-------	340	-------	489
Nickel residues	2,052	252	1,948	282
Total (nickel-base)[1]	3,684	2,750	3,708	1,934

[1] Nickel silver is excluded from total because it is copper-base scrap, although containing considerable nickel.

TABLE 6.—*Nickel recovered from nonferrous scrap processed in the United States by form of recovery*

[Short tons]

Form of recovery	1961	1962	1963
As metal	1,210	1,252	1,619
In nickel-base alloys	1,824	2,037	2,079
In copper-base alloys	2,640	2,552	2,679
In aluminum-base alloys	863	901	998
In ferrous and high-temperature alloys [1]	2,059	2,154	1,087
In chemical compounds	2,092	2,212	2,301
Total	10,688	11,108	10,763

[1] Includes only nonferrous nickel scrap added to ferrous and high-temperature alloys.

RESERVES

The largest known potential resource of nickel in the world, conservatively estimated at 17 million tons of nickel content, is in the nickel-bearing laterite and serpentine ores in Cuba. The second largest known reserve is in New Caledonia with an estimated nickel content of

16 million tons. Reserves of proven and indicated nickel in the sulfide ore deposits of the Sudbury district and the newly-developed Manitoba areas in Canada total about 6 million tons of nickel content.

As of early 1964, reserves of proven and indicated nickel-bearing material in the United States were placed at about 71 million tons with a nickel content of approximately 500,000 tons. Of this amount, 360,000 tons of nickel was in silicate and nickeliferous iron ores and 140,000 tons in sulfide ores. About one-half of the sulfide ore is in Alaska. Most domestic sulfide deposits are too small to warrant establishment of a nickel smelting industry. Table 7 gives ore reserves of the major Canadian producers in 1963.

TABLE 7.—*Estimated reserves of major Canadian producers in 1963*

[Million tons]

Company	Ore	Nickel content (percent)
International Nickel Co. of Canada, Ltd.: Proven ore reserve	302	1.6
Falconbridge Nickel Mines, Ltd.:		
Proven ore reserve	27	1.6
Indicated ore reserve	24	1.2
Sherritt Gordon Mines, Ltd.: Indicated ore reserve	12	.9

Nickel-bearing laterite deposits are abundantly distributed in a wide belt of tropical and semitropical countries around the world. Large deposits are known in Cuba, Brazil, Venezuela, Puerto Rico, the Dominican Republic, Greece, Pakistan, India, the Malagasy Republic, the Republic of the Philippines, the Republic of Indonesia, and the French Pacific Islands (New Caledonia). Some of the largest deposits, such as those in the Republic of the Philippines, may contain more than 1 billion tons of potential ore (*1*).[2] The prospect for the discovery of additional nickeliferous laterite deposits is good, since many areas in the equatorial regions where laterite is found are relatively underdeveloped and have not been extensively prospected.

Puerto Rico has nickeliferous laterite and serpentine deposits estimated at least 100 million tons of ore with an average nickel content less than 1 percent. It is estimated that the Republic of the Philippines has a laterite reserve of about 120 million tons of these ores and a larger tonnage of lower grade nickel ore. Other nickel resources amenable to large-scale development are in Central and South America, Indonesia, and Africa.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

Nodules on the ocean floor represent another potential source of nickel. Manganese dioxide nodules scattered over large areas also contain nickel, cobalt, copper, and iron.

SOURCES OF STATISTICAL INFORMATION

Annual data on production of nickel ore are obtained from domestic producers by the Bureau of Mines. Data on annual consumption by form and end use, and on stocks by form are obtained from about 1,030 consumers which account for about 99 percent of total consumption reported in 1963; corresponding monthly data are obtained from 200 consumers which account for about 94 percent of the consumption reported in 1963. World production data are compiled from Foreign Service dispatches and official publications of foreign countries, and figures on foreign trade are obtained from the Bureau of the Census.

PRODUCTION, CONSUMPTION, AND TRADE

Free world annual production of nickel increased from about 10,000 tons in 1900 to a record high of 301,000 tons in 1961 when the U.S. Government was purchasing it for the national stockpile. The total free-world nickel production in 1962 and 1963 was 287,000 and 271,000 tons, respectively.

Of the free-world nickel production in 1963, Canada produced 81 percent; New Caledonia, 12 percent; and the United States, 4 percent. Table 8 gives the world production of nickel from 1959 to 1963. Despite the decline in nickel production in 1963, U.S. industrial consumption was approximately 125,000 tons, about a 5-percent increase above the 1961–62 levels.

Of the total United States imports in 1963, 91 percent was nickel metal and 8 percent was nickel oxide. Canada provided 91 percent of the total imports and Norway, 7 percent. Since Norway's raw materials originated from Canada, the United States, in effect, imports 98 percent of its nickel from Canada. France and other countries provide the remaining 2 percent.

Exports of nickel-bearing material by the United States have been increasing. In 1963 this country exported 61,000 tons of nickel-bearing materials consisting principally of nickel and nickel-alloy scrap. Compared with the 1962 figure, this was an increase of 120 percent. Shipments to Japan were 67 percent of the 1963 total; to Canada, 12 percent; to Italy, 11 percent; and to Sweden, United Kingdom, and West Germany, 3 percent each.

TABLE 8.—*World mine production of nickel*

[Short tons of nickel content]

Country	1954–58 (average)	1959	1960	1961	1962	1963
Albania	1,000	1,800	2,700	3,300	3,300	3,300
Canada [1]	168,448	186,555	214,506	232,991	237,044	219,941
Cuba	17,554	19,858	[2] 14,147	[3] 16,320	[3] 18,302	[3] 18,400
Finland	120	416	2,495	2,377	2,859	3,402
New Caledonia [4]	20,255	28,810	43,325	48,600	32,400	32,200
Poland	1,219	1,405	1,382	1,453	1,458	[3] 1,400
Republic of South Africa	2,813	[3] 2,900	[3] 3,200	[3] 2,900	[3] 2,700	[3] 2,700
U.S.S.R.[3]	51,800	60,000	64,000	83,000	90,000	90,000
United States	6,634	11,606	12,530	11,176	11,217	11,432
Other countries	1,157	650	715	883	1,720	1,225
Total [3]	271,000	314,000	359,000	403,000	401,000	384,000

[1] Comprises refined nickel and nickel in oxide produced and recoverable nickel in matte exported.
[2] Exclusive of unkown tonnage produced and stored at Nicaro since Sept. 20, 1960.
[3] Estimate.
[4] Comprises nickel content of matte and ferronickel produced in New Caledonia plus estimate of recoverable nickel in ore exported. Mine production (nickel content of ore) was as follows: 1954–58 (average) 27,650 tons; 1959, 36,200 tons; 1960, 59,000 tons; 1961, 58,800 tons; 1962, 37,500 tons; and 1963, estimated, 59,100 tons.

The duty on nickel metal imported into the United States is 1.25 cents per pound. Nickel ore, matte, slurry, oxide powder, and oxide sinter enter duty free.

TABLE 9.—*Nickel (exclusive of scrap) consumed in the United States, by uses*

[Short tons]

Use	1961	1962	1963
Ferrous:			
Stainless steels	34,213	29,711	34,140
Other steels	18,238	18,608	19,727
Cast irons	4,649	5,503	5,901
Nonferrous [1]	28,789	28,215	24,794
High-temperature and electrical-resistance alloys	11,294	12,862	13,505
Electroplating:			
Anodes [2]	15,737	16,953	18,621
Solutions [3]	770	904	1,050
Catalysts	1,519	1,566	1,613
Ceramics	366	439	554
Magnets	773	910	777
Other	2,167	3,006	3,796
Total	118,515	118,677	124,478

[1] Comprises conper-nickel alloys, nickel silver, brass, bronze, beryllium alloys, magnesium and aluminum alloys; Monel, Inconel, and malleable nickel.
[2] Figures represent quantity of nickel used for production of anodes, plus cathodes used as anodes in plating operations.
[3] Figures do not cover all consumers.

STRATEGIC CONSIDERATIONS

In 1963, total domestic primary and secondary nickel production was approximately 22,000 tons, about 19 percent of U.S. consumption. There is little likelihood of improvement in this domestic supply position. Since nickel is a strategic and critical metal, it has been acquired for the national stockpile to insure a supply in the event of a national emergency. As of June 30, 1964 inventories totaled 219,278 tons of nickel, 166,914 tons in the national (strategic) stockpile and 52,364 tons in the Defense Production Act (DPA) inventory. Of the total amount, 50,000 tons was declared within the objective, and 169,278 tons was declared in excess. In addition to the inventories of the Federal Government, consumer stocks at yearend, 1963 amounted to 17,191 tons, up approximately 3,700 tons from that of yearend, 1962.

Alloy steels of 1 percent to about 5 percent nickel are used for military aircraft, ships, vehicles, weapons, ammunition and other military hardware. Stainless steels containing 7 percent to 30 percent nickel find a use in the production of aircraft engines, airframes, and ocean vessels. Nickel-base alloys, which are mainly high-temperature materials, are specified chiefly in gas turbines, jet engines, and other applications requiring alloys with high mechanical strength at elevated temperatures. Corrosion resistant nickel-base alloys are used in ships, storage tanks, and various processing equipment. A number of nickel alloys are used in plants and equipment in the metalworking, mining, oilfield, power, chemical, railroad, and other industries.

The United States depends almost entirely on the Canadian supply and to a lesser extent on the New Caledonian source for its needs of nickel. Since the seizure of American owned nickel plants by the present Cuban government, nickel shipment from Cuba to the United States has been suspended. Potential nickel supplies may come from Central and South American countries, the Caribbean area, the Philippine Islands, India, Indonesia, and Federation of Malaysia.

GOVERNMENT PROGRAMS

In October 1963 an Interdepartmental Disposal Committee was charged with the responsibility for determining criteria and procedures for the development of long-range programs to dispose of surplus material in the Government stockpiles. In November, work was begun on plans to dispose of nickel.

At the end of 1963 only the Hanna Nickel Smelting Co. held an unfulfilled contract to deliver nickel to the stockpile. However, by mutual consent, deliveries had been suspended.

The Government offers financial assistance up to 50 percent of allowable costs for exploration for mineral reserves of nickel. No assistance contracts are in effect.

PRICES

The price of nickel metal rose in June 1961 from its 5-year plateau of 74 cents per pound to 81¼ cents and declined again in May 1962 to 79 cents, its price at the close of 1963. Except for shaded prices of oxide in 1958 through 1960 the price of oxide nickel remained 3¾ cents per pound below that of the metal, but 1¼ cents reflects a U.S. import duty on the metal. Table 10 gives nickel prices for the metal and the oxide from 1951 through 1963.

TABLE 10.—*Prices per pound of nickel metal and nickel oxides in the United States*

Year	Date of change in price	Nickel metal, f.o.b. Port Colborne, Ontario, duty included	Nickel oxide sinter (nickel content) f.o.b. Copper Cliff, Ontario, no duty	Cuban nickel oxides (nickel content) f.o.b. Philadelphia	
				Powder	Sinter
1951	June 1	$0.56½	$0.52¾	$0.50¾	--------
1952	Unchanged	.56½	.52¾	.50¾	--------
1953	Jan. 14	.60	.56¼	54¼	--------
1954	Nov. 24	.64½	.60¾	.59½	$0.60¾
1955	Unchanged	.64½	.60¾	.59½	.60¾
1956	Dec. 6	.74	.70¼	.69	.70¼
1957	Unchanged	.74	.70¼	.69	.70¼
1958	do	.74	[1] .696	.69	--------
1959	do	.74	.696	.69	--------
1960	do	.74	.696	.69	--------
1961	June 30	.81¼	.77½	--------	--------
1962	May 24	.79	.75¼	--------	--------
1963	Unchanged	.79	.75¼	--------	--------

[1] Price f.o.b. port of entry, reduced by International Nickel Co. of Canada, Ltd., to compete with Cuban nickel oxide.

TAXES

Domestic nickel producers are granted a depletion allowance of 23 percent on income from domestic production and 15 percent on income from foreign production.

In addition to a 15 percent depletion allowance (of salable value of minerals), taxable income of operations outside the United States and within the Western Hemisphere are taxed at 14 percentage points below the U.S. corporate income tax rate. With an approximate rate of 48 percent for domestic operations, the rate for Western Hemisphere trading corporations is about 34 percent.

RESEARCH

The Bureau of Mines conducts research projects related to the conservation and production of nickel, which range from mineral exploration to electrolytic recovery of refined nickel (*2*, *3*, *6*, *8*, *13*). It makes theoretical studies of basic nature (*17*, *22*), including the properties of nickel and its alloys (*5*, *21*), and it investigates analytical methods (*10*, *19*). Much effort has been devoted to the beneficiation of ores (*18*) and to the recovery of nickel from them (*1*, *7*, *12*, *16*). The recovery of nickel from scrap receives attention (*9*, *11*).

The International Nickel Co. of Canada, Ltd. maintains facilities in which research is directed largely toward immediate commercial objectives, but basic studies are carried out. The company issues The Nickel Bulletin which contains abstracts of recent literature pertaining to nickel.

Falconbridge Nickel Mines, Ltd. officially opened a $1 million metallurgical research laboratory at Thornhill, Ontario, in 1963 with a staff of 50 scientists, engineers, and technicians. The Sherritt Gordon Mines, Ltd. has research laboratories in its metallurgical plant at Fort Saskatchewan, Alberta, Canada. A great many articles have been published dealing with chemical methods of extracting metals from ores, including laterites, and dealing with the production of metal powders and their fabrication into dense strip.

The Defense Metals Information Center, Columbus, Ohio, publishes reports pertaining to the properties of nickel and its alloys (*4*, *14*, *15*).

OUTLOOK

Total free world nickel producing capacity in 1963 was conservatively placed at about 330,000 tons annually, exceeding the current annual consumption rate in the free world by about 62,500 tons. The outlook is for continued free world excess capacity to produce nickel. There are ample reserves of sulfide ores in Canada and of silicate ores throughout the Tropics. There are feasible ways to exploit low-tenor ores of each type which will enable producers to meet any forseeable level of world demand. This may be expected despite the fact that, currently, increasing deliveries of nickel are steadily correcting the 20 to 25 percent excess capacity that was reported at the beginning of 1963.

The outlook on consumption of nickel for the United States and the rest of the free world is for continued steady increases resulting from general economic growth and from the development of new uses. It is probable that this country will continue to consume about 50 percent of the free world total, at least in the foreseeable future. The rate of increase in nickel use has in the past been held down by substitution of other metals as well as by replacing nickel-bearing materials of higher nickel content with lower content alloys. It is expected these practices will continue. However, countering this trend of reduction in the use of nickel by substitution is sales advertising by producers directed toward the ultimate consumer.

The recent discovery of huge nickel sulfide deposits in the Thompson, Manitoba, area and elsewhere in Canada has probably assured the continued dominance of Canadian sulfide ore as the major source of the free world nickel for many years. Intensive prospecting in other areas of Canada may result in the discovery of other nickel ore deposits. Thus, barring a major increase in the consumption rate, the United States and the rest of the free world is assured of adequate supplies of nickel from Canada for the next 50 to 70 years.

The prospect of finding nickel ore in large quantities in the United States is poor. With the possible exception of Alaska, most of the promising areas of the United States have been well prospected, and although a number of relatively small, low-grade deposits have been found, no commercial deposits have been developed except that at Riddle, Oreg., now mined by the Hanna Mining Co. The reserve at the Riddle mine is expected to last about 15 more years at the capacity production of about 14,000 tons per year with little prospect of finding more ore nearby.

PROBLEMS

Some of the unsolved problems in the technology of nickel are as follows: lack of knowledge of the theoretical basis of its metallurgy; need for an economic way to separate nickel and cobalt; economical methods to recover nickel from silicate and lateritic ores and from other minerals with a low nickel content; and economical reclamation of nickel from high-temperature and cryogenic alloy scrap, spent catalysts, and other nickel alloy materials.

Although nickel is widely used in many alloys to impart toughness, corrosion resistance, low-temperature ductility, and to improve high-temperature properties, the development of alloys is often done by trial-and-error procedures rather than by more scientific methods based on knowledge of the basic mechanisms of the alloying process. There is, then, need for more fundamental research in this field not only to gather information about various alloying processes, but more importantly, to synthesize the gathered information into a more unified explanation of these processes. With greater elucidation of the fundamental alloying mechanisms, the formulation of new alloys with the desired physical and chemical properties would be based on more reliable information, and results would be more certain.

Nickel ores usually contain some cobalt which is difficult to remove because of the chemical similarity of the two metals. Currently used methods are relatively complicated and often involve large circulating loads. The problem may be approached by three methods: separation of the two metals from the ore by the preparation of separate concentrates, separation during smelting by slagging off the cobalt, and separation from the electrolyte during electrolytic refining. Although the very close similarity in the chemical and physical behavior of nickel and cobalt minerals and compounds poses formidable difficulties to any of these approaches, some success has been attained recently in all of them. The third approach seems to be the most promising.

The problem with silicate and nickeliferous lateritic ores is twofold. In the first place, no economical method has yet been found for producing a physical concentrate from these minerals. This normally means that smelting or leaching plants must be built close to the ore deposits, since it is usually uneconomic to transport the ore over long distances due to its relatively low nickel and high moisture content. An intensive study of the application of mineral dressing techniques to these and other relatively low-grade minerals might lead to the development of a method by which a separation of some of the constituents could be made.

Secondly, present processes for the exploitation of silicate and nickeliferous laterite ores do not make full use of the potential of these ores as sources of iron, cobalt, and other contained metals. The ammonia leach process used at the formerly U.S. Government-owned Nicaro plant in Cuba recovered less than 80 percent of the nickel and less than 10 percent of the cobalt. The tailings were too high in nickel, chromium, and cobalt to be suitable for use as iron ore.

The acid leach process used at Freeport Sulphur Company's former plant at Moa Bay recovered over 95 percent of the nickel and cobalt, and the 50-percent iron content of the tailings was also to have been recovered by a direct reduction process. The process, however, is not usable on the serpentine fraction of the lateritic ores, which may make up one-third of the total weight of the ore and may be the richest in nickel content.

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NITROGEN

By Richard W. Lewis [1]

NITROGEN has a key role in the life cycle of plants and animals. When man devised methods to "fix" atmospheric nitrogen he achieved independence from the inadequate supply of naturally derived nitrogenous materials. The atmosphere is the main source of nitrogen supply. Other sources include natural nitrates, coal, and natural organic materials, such as cotton seed, tankage, bone meal, and guano.

Ammonia, the most important nitrogen compound, is produced synthetically in vast quantities by reacting nitrogen with hydrogen in the presence of a catalyst. It is the basic compound from which a host of other nitrogen compounds are made. Most of the nitric acid consumed in the United States is made by oxidizing anhydrous ammonia.

The fertilizer industry is the largest consumer of nitrogen compounds. Ammonium sulfate, ammonium nitrate, and ammonium phosphate are components of mixed fertilizers and are produced by neutralizing the respective acids with ammonia. These compounds, as well as ammonia, both anhydrous and in solution, are sometimes applied directly to the soil or to irrigation waters to supply nitrogen to growing crops.

The largest single industrial use of ammonia is for explosives. It is the basic ingredient for the production of sodium nitrate, ammonium nitrate, nitrocellulose, nitroglycerine, trinitrotoluene (TNT), and other explosives.

The only important commercial source of natural nitrates is Chile. Strong competition in the world markets by synthetically produced nitrates has made it increasingly difficult to mine and sell natural nitrates profitably.

Nitrogen as a liquid or as a gas has shown a rapid increase in industrial importance. Large volumes are produced annually in air-separation plants by a simple process of liquefaction and fractional distillation of the atmosphere.

The reserves of nitrogen in the atmosphere, coal deposits, and natural mineral deposits assure ample supplies for all time. The quantity available for agricultural and industrial uses is limited only by the production capacity of the processing facilities.

The demand for nitrogenous fertilizer materials will continue upward to assist in meeting the increasing needs for agricultural products. Further growth is expected in the use of ammonium nitrate for field-compounded explosives. Also, increased use by industry of high-purity nitrogen, liquid and gas, is anticipated.

Problems of the nitrogen industry include providing an adequate supply of nitrogen compounds to meet fluctuating seasonal demands and reducing operational costs to meet foreign competition.

BACKGROUND

SIZE AND ORGANIZATION OF THE INDUSTRY

Until the 18th century, organic nitrogen materials, primarily animal and plant wastes produced at or near the point of use, accounted for supplemental nitrogenous plant food. From the 18th century until the 1920's, the nitrate deposits of Chile were virtually the only commercial source of nitrogen. Since then, the chemical industry, by nitrogen fixation, has supplied the major part of the world's nitrogen requirements.

The four main sources of nitrogen today are—(1) the atmosphere, (2) coal, (3) natural nitrates, and (4) organic materials.

The first commercial nitrogen fixation plant was established in Norway about 1900 and used the arc process. Nitrogen and oxygen in the air were combined by an electric arc to form nitrogen oxides, which were absorbed in water to form nitric acid. The cyanamide

[1] Commodity specialist.

process, first used commercially in Italy in 1906, makes calcium cyanamide by reacting calcium carbide, prepared from coke and limestone, with atmospheric nitrogen. The Haber-Bosch process, developed in Germany between 1905 and 1913, produces synthetic ammonia by combining nitrogen and hydrogen in the presence of a catalyst at elevated temperatures and pressures. Research in every major country was stimulated by the success of the Haber-Bosch process, and a number of variations were developed to produce ammonia from nitrogen and hydrogen.

The first successful domestic synthetic ammonia plant was built at Syracuse, N.Y., by the Atmospheric Nitrogen Corp. in 1921. A modification of the Haber-Bosch process was used. This plant was followed by others which soon were contributing large quantities of nitrogen compounds to supply the growing demand. To insure adequate supplies of nitrogen compounds during World War II, the Government constructed 10 synthetic ammonia plants with a total rated capacity of 863,000 short tons of nitrogen equivalent per year. The plants were operated by the Government in the latter part of the war, after which all except the Tennessee Valley Authority (TVA) plant at Muscle Shoals, Ala., were sold or leased and now are operated by private industry to produce nitrogen compounds.

The synthetic nitrogen compound industry in the United States was expanded rapidly between 1951 and 1958. At the beginning of 1959 the industry was comprised of more than 40 companies and the TVA, which were operating about 55 synthetic ammonia plants in 28 States and Puerto Rico. Total annual rated capacity was nearly 5 million short tons of nitrogen equivalent. In addition, there were about 80 coking plants in 21 States with a total productive capacity of more than 250,000 tons of nitrogen equivalent per year as a byproduct. During the next 5 years an even greater expansion of the industry took place, and by December 31, 1963, 79 ammonia plants were in operation, having a combined capacity of about 8.2 million short tons per year. The production of byproduct ammonia from coking plants, however, declined slightly. In 1963, 59 of the 66 coking plants in operation recovered a total of 185,301 tons of ammonia, of which 86 percent was converted into ammonium sulfate.

The growth of the elemental nitrogen (gaseous and liquid) industry has been phenomenal. The average annual domestic production for 1953–57 was 141,000 short tons, whereas in 1963 over 2 million tons was produced. This production did not include the output of a large number of small "make it yourself" units in use throughout the Nation.

DEFINITIONS OF TERMS, GRADES, AND SPECIFICATIONS

Nitrogen is a colorless, odorless, and generally inert gaseous element making up 78 percent of the air by volume. This nitrogen is referred to as atmospheric nitrogen and is represented chemically by "N."

Fixed nitrogen is nitrogen that is chemically combined with one or more other elements and is present in all living things, both plant and animal. Sodium nitrate ($NaNO_3$) or soda-niter and potassium nitrate (KNO_3), sometimes referred to as niter or saltpeter, are the only natural occurring nitrogen minerals of importance. (*12*).[2]

Although more than 250,000 nitrogen-containing compounds are known, only a few are important in the fertilizer and chemical industries. These include anhydrous ammonia (NH_3), ammonium nitrate (NH_4NO_3), ammonium sulfate ($(NH_4)_2SO_4$), monoammonium phosphate ($NH_4H_2PO_4$), diammonium phosphate ($(NH_4)_2HPO_4$), calcium cyanamide ($CaCN_2$), nitric acid (HNO_3), urea (NH_2CONH_2), and the two natural nitrates. Recently synthetic potassium nitrate has become more prominent.

Aqua ammonia, as the name implies, is anhydrous ammonia dissolved in water to form ammonium hydroxide (NH_4OH). Commercial grades usually contain 20 to 25 percent nitrogen.

Grade regulations for mixed fertilizers, including nitrogenous fertilizers, are under State control. Summaries of these regulations are published annually (*2*). Grades and purity specifications for nitrogen and nitrogen compounds for industrial use are varied and established by the individual manufacturer.

TECHNOLOGY

Nitrogen Fixation Processes

The atmosphere is the major source material from which nitrogen is extracted and "fixed" for use in the fertilizer, chemical, and explosive industries. Three basic processes may be used to fix atmospheric nitrogen: The arc process which produces dilute nitric acid; the cyanamide process which produces calcium cyanamide; and the synthetic ammonia process which produces ammonia. Other methods were developed for fixing nitrogen but were little used and are of no importance.

The arc method (*7*) has no commercial importance in the United States chiefly due to

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

the large investment and the electrical energy requirements per ton of product. However, it uses directly the cheapest and most plentiful of raw materials, air and water, and produces directly a very desirable form of fixed nitrogen, nitric acid.

The cyanamide process (*6*) involves four steps to produce calcium cyanamide: The production of lime by calcining limestone; the manufacture of calcium carbide in an electric-arc furnace by reacting lime with coke; the separation of nitrogen from the atmosphere by the fractionation of liquid air; and the reaction of the calcium carbide with the nitrogen to produce cyanamide. Calcium cyanamide, early in the century was used extensively as a fertilizer. Today, however, it represents only about 2.5 percent of the nitrogenous fertilizers consumed in the world.

The synthetic ammonia method is currently by far the most important and most used method. Although there are several processes in general use today, all may be considered as modifications or variations of the original Haber-Bosch process. They have in common the following three main steps:

1. Preparation of hydrogen and nitrogen.
2. Purification and compression of the gases.
3. Conversion of the gases into ammonia.

Nitrogen necessary for ammonia synthesis may be obtained from producer gas, or when hydrogen is cheap, sufficient air can be mixed with hydrogen and the oxygen burned out to give a hydrogen-nitrogen gas mixture. The most used method, however, is by fractional distillation of liquid air which produces a nitrogen of high purity.

Hydrogen is obtained principally from natural gas in the United States but also is produced from coal by water-gas reaction, water by electrolysis, coke-oven gases, and byproducts of caustic-chlorine and ethylene production and petroleum refining.

The process of ammonia synthesis consists essentially of passing nitrogen and hydrogen over a catalyst (usually iron oxide) at high pressures and temperatures. The product is ammonia, mixed with nitrogen and hydrogen, from which ammonia is recovered by absorption or refrigeration. Unreacted nitrogen and hydrogen are returned to the process.

Process requirements for manufacturing ammonia and selected nitrogen compounds for raw materials, process and cooling water, power, and catalysts have been published by the Bureau of Mines (*5*). For example, about 1,500 kilowatt-hours of electricity is required to produce 1 ton of ammonia, compared with 5,100 kilowatt-hours to produce 1 ton of elemental phosphorus.

Coking-Plant Nitrogen

The gas from coking coal is a mixture of ammonia, carbon dioxide, hydrogen, methane, water vapor, coal tar, and small quantities of various hydrocarbons. After passing through a tar separator, the gas is passed through water, sulfuric acid, or phosphoric acid to recover aqua ammonia, ammonium sulfate, or ammonium phosphate (*13*, *14*).

Natural Nitrate Deposits

Small deposits of soluble nitrate minerals are widely distributed in the United States. Nitrate deposits have been found in 23 States. Most occurrences are in the arid and semiarid parts of the Western United States. Three types of nitrate deposits are known—cave, caliche, and playa. Cave nitrates are the most numerous and contain the widest variety of nitrate salts, including potassium, sodium, calcium, and (more rarely) magnesium and ammonium. Caliche and playa deposits are composed chiefly of sodium nitrate. The domestic deposits are discussed in detail in various Geological Survey reports (*4*, *8*, *10*, *11*).

Nearly all the known nitrate deposits in the United States are too small and low-grade to support a domestic nitrate industry, although small-scale production has been reported. Production from one cave deposit began early in 1957 in the Grand Canyon, Ariz. The guano was mined by a suction hose and carried across the canyon on a 1½-mile aerial tramway. There, it was packaged for sale as an organic nitrogenous fertilizer. This venture is not currently in operation.

The only commercially important large nitrate deposits in the world are in Chile, in an area 10 to 50 miles wide and 450 miles long between the Coast Range and the Andes Mountains in northern Chile. The nitrate-bearing ores contain 5 to 30 percent sodium nitrate and occur in slightly dipping beds a few inches to several feet thick overlain by an overburden of loose sand and gravel or consolidated conglomerate. The nitrate ore is mined by both hand and mechanical mining. Open-pit mining usually is employed, but some underground mining is done when the overburden exceeds 30 feet in thickness.

There are two main methods of extracting the nitrate from the ores—the Shanks process and the Guggenheim process. Both are solution and recrystallization methods. The Shanks process was the first method used to recover marketable nitrate and was applied only to ore containing more than 15 percent $NaNO_3$. The Guggenheim process, which was developed in 1925, permitted treating ore down to 8 per-

cent $NaNO_3$, with recovery of nearly 100 percent of the nitrate, by using countercurrent leaching at a lower temperature. The Guggenheim process requires closer temperature control and more plant facilities than the Shanks process.

With the development of synthetic processes, many chemical products became competitors of Chilean nitrate; however, natural nitrates contain minor quantities of magnesium, iodine, boron, calcium, potassium, lithium, and strontium, which contribute slightly to the minor plant-food-element supply of the soil. Despite available and cheaper synthetic nitrogen, sales of Chilean nitrate have been maintained relatively high.

Guano deposits in Peru, an important source of nitrogenous materials before 1900, are now controlled by the Peruvian Government. Guano obtained from them is consumed largely in Peru.

Organic Nitrogen

Raw materials for the organic nitrogen industry include byproducts of slaughter houses (blood), rendering plants (animal tankage), tanneries (process tankage), fish processing plants (fish scrap), cottonseed and other seed mills, and processed sewage. Substantial quantities of nitrogen also are added to the soil through manures and cover crops.

USES

Nitrogen compounds are essential to the fertilizer and explosives industries and have many important applications in the chemical industry. Ammonia is the major nitrogen product, and many other compounds and salts are made from it for use in the fertilizer, chemical, and explosives industries.

The nitrogenous material used for fertilizers can either be applied directly or as mixed fertilizer containing two or more plant-food elements. The principal compounds now used as fertilizer, in order of importance, are ammonium nitrate and ammonium nitrate-limestone mixtures, sodium nitrate, anhydrous and aqua ammonia, ammonium sulfate, calcium cyanamide, calcium nitrate, and urea.

Industrial uses of nitrogen compounds are many and varied. Ammonia is used in manufacturing paper, plastics, and synthetic fibers and in refrigeration, metal treatment, water purification, and oil refining. Nitric acid is one of the more valuable chemical reagents. It is an important solvent and basic chemical and is used extensively in making explosives and dyes. Many other nitrogen compounds are important to both the fertilizer and chemical industries, one of the most interesting being the increasing use of prilled ammonium nitrate in explosives. However, most of the domestic production of ammonium nitrate is used in fertilizer.

Elemental nitrogen has a wide diversity of uses in industry including chemicals, drugs, electronics, food processing, metals, and oil-well drilling.

The ammonia industry consumes the largest amount of nitrogen. This amount, however, is not reported in the production of pure nitrogen since it is used captively as produced.

The largest use of pure nitrogen is as a blanketing gas medium in the electronic and metal industries. Liquid nitrogen consumption is increasing in food processing and as a refrigerant for food transportation. Also, more liquid nitrogen is being consumed each year for use in rockets and missiles.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Nitrogen production from coking operations, less than 5 percent of the U.S. output of inorganic nitrogen compounds, is directly geared to the steel industry. The demand for steel governs the quantity of nitrogen made available from this source. The proportionate output of aqua ammonia, ammonium sulfate, and ammonium phosphate depends on the requirements of the fertilizer market.

The quantities of nitrogen, phosphate rock, and potash consumed in mixed fertilizers are closely related.

Elemental nitrogen production is closely associated with oxygen in that the two are obtained simultaneously from the atmosphere in air-separation plants.

ALTERNATE MATERIALS

There is no substitute for nitrogen as a plant food. However, there are many nitrogenous fertilizers from which to choose—price, physical characteristics, and agronomic factors being considered. There is no substitute for nitrogen in the production of ammonia which is the major consumer.

Although a number of explosive compounds containing no nitrogen are known and used, it would be difficult to substitute for all nitrogenous explosives.

Some substitutions are possible, although not economical, for elemental nitrogen in a few of its uses. Helium or argon may be substituted for nitrogen as a blanketing gas in some metallurgical operations.

RESERVES

The mass of the atmosphere has been estimated at more than 5 quadrillion tons containing about 4 quadrillion tons of nitrogen, or about 148,000 tons for every acre of land area. Each day, lightning fixes about 60,000 tons of nitrogen, which reaches the earth in the form of nitric or nitrous acids; however, most of this tonnage falls on nonagricultural areas. The nitrogen content of the air is replenished constantly (primarily through decomposition of organic materials), providing a never-ending source.

The quantity of nitrogen in coal ranges from less than 1 to 3 percent. The domestic recoverable reserve of coal is estimated at about 830 billion tons, containing 5 to 25 billion tons of nitrogen. At present, only about one-sixth of the total nitrogen in coal is recoverable. The nitrate reserve in Chile is estimated to be slightly under 1 billion tons and is the only important commercial source of natural nitrates in the world.

SOURCES OF STATISTICAL INFORMATION

World statistics on fertilizer materials, including nitrogen compounds, usually are collected on a crop-year basis. The crop-year is not the same for all countries; however, most countries report data for 12-month periods ending June 30.

Statistics on estimated world production and consumption of agricultural nitrogen are compiled and published by the Food and Agricultural Organization of the United Nations (*3*). Aikman (London), Ltd., compiles and publishes estimated world production and consumption data on agricultural and industrial nitrogen compounds (*9*). Both reports are for crop-years ending June 30. A canvass on consumption of nitrogenous fertilizers is conducted by the Agricultural Research Service, Department of Agriculture, and statistics are published for annual periods ending June 30 (*15*). Data on production, shipments, imports, and exports of certain nitrogenous fertilizers and chemicals are collected by Bureau of the Census. Some data are published monthly, and all are published on a calendar-year basis (*1*).

Statistics on production, sales, and stocks of ammonia, ammonium sulfate, and ammonium phosphates at coke-oven installations are collected and published monthly by the Bureau of Mines. Data from all sources are published in the Nitrogen chapter of the Minerals Yearbook, volume I, on whatever basis the material is available.

Statistics on nitrogen compounds in explosives are included in the Bureau of Mines annual Mineral Market Report, Consumption of Industrial Explosives. The Bureau of the Census publishes periodic data on explosive materials in Industrial Organic Chemicals, Census of Manufactures.

PRODUCTION, CONSUMPTION, AND TRADE

Table 1 gives U.S. production of nitrogen from synthetic ammonia plants, coking plants, and air-separation plants. Major nitrogen compounds produced during 1959–63 are given in table 2. Imports and exports of nitrogen compounds are shown in table 3. Table 4 presents world production and consumption of nitrogen compounds for both fertilizer and technical purposes for the fiscal years ending June 30, 1959–63.

From 1959 to 1963 ammonia nitrogen production increased 68 percent, while elemental nitrogen became the fastest growing industrial gas with production in 1963 nearly eight times that of 1958.

Peacetime consumption of fixed nitrogen has been about 75 percent for agricultural uses and 25 percent for industrial uses. In 1963, it is estimated that 80 percent of consumption went

TABLE 1.—*Nitrogen production in the United States*

[Short tons of contained nitrogen]

	1959	1960	1961	1962	1963 [1]
Anhydrous ammonia: Synthetic plants [2]	3,717,186	3,962,272	4,282,160	4,778,106	5,465,757
Ammonia compounds, coking plants:					
Ammonia liquor	12,098	12,241	10,990	11,166	11,873
Ammonium sulfate	131,613	134,034	125,951	124,112	131,034
Ammonium phosphates	9,946	9,769	10,111	6,909	8,283
Total	3,870,843	4,118,316	4,429,212	4,920,293	5,616,947
Nitrogen gas [2]	543,875	724,724	1,045,357	1,682,643	2,032,006

[1] Preliminary figures.

[2] Bureau of the Census Current Industrial Reports.

TABLE 2.—*Major nitrogen compounds produced in the United States*

[Thousand short tons]

Compounds	1959	1960	1961	1962	1963
Anhydrous ammonia	4,520	4,818	5,207	5,810	[1] 6,646
Ammonium chloride [2]	26	28	25	23	[1] 25
Ammonium nitrate [2]	2,857	3,122	3,235	3,406	3,939
Ammonium sulfate [2]	1,714	1,492	1,545	1,697	1,785
Ammonium phosphate [3]	691	984	1,237	1,624	2,635
Nitric acid [2]	3,074	3,315	3,380	3,670	4,197
Urea [4]	631	735	922	1,020	[1] 1,066

[1] Preliminary figure.
[2] Bureau of the Census Current Industrial Report M28A
[3] Estimates, 1961, 1962, 1963 revised.
[4] U.S. Tariff Commission.

into fertilizer materials. World consumption during 1963 is estimated at 17.5 million short tons with the United States consuming slightly more than 5 million tons. Thus, there has been no appreciable overproduction, and further expansion of the productive facilities are quite likely. Most of the increased demand for nitrogen compounds has been due to increased use of fertilizers with a larger proportionate use of nitrogen.

No consumption data are available for liquid and gaseous nitrogen, but it can be assumed that practically all produced was used. The spectacular rise in demand for pure nitrogen is due chiefly to the growth of markets that did not exist a few years ago. Greater amounts are being used annually for such uses as frozen food processing and transportation, oil well stimulation, and in environmental testing of space vehicles and components.

In general, the U.S. foreign trade situation is slowly changing due to heavy foreign competition. The trend during the past 5 years has been for increased imports and decreased exports. The increased imports are especially

TABLE 3.—*U.S. imports for consumption and exports of major nitrogen compounds* [1]

[Short tons]

Compounds	1959	1960	1961	1962	1963
Imports:					
Industrial chemicals: Ammonium nitrate	----------	----------	106	442	58
Fertilizer materials:					
Anhydrous ammonia	([2])	([2])	([2])	([2])	17,453
Ammonium nitrate, containing over 32 percent nitrogen	[3] 341,037	172,366	156,650	216,153	[4] 161,948
Ammonium nitrate mixtures, containing 32 percent and less nitrogen including ammonium nitrate-calcium nitrate mixtures except solutions	----------	73,193	92,033	122,006	[4] 45,614
Ammonium phosphates	215,707	119,937	112,993	131,578	129,710
Ammonium sulfate	217,473	211,351	246,866	244,998	234,507
Calcium cyanamide	58,400	44,100	41,987	36,946	28,896
Calcium nitrate	68,849	62,023	73,737	58,167	41,675
Nitrogen solutions [5]	----------	50,174	64,269	68,645	77,920
Nitrogen fertilizer materials, synthetic, not elsewhere specified	22,440	47,475	47,280	58,600	[6] 50,849
Potassium nitrate, crude	473	635	1,962	3,187	4,446
Potassium-sodium nitrate mixtures, crude	36,468	18,632	13,801	27,301	38,080
Sodium nitrate	461,765	355,112	494,345	434,004	119,546
Urea, not elsewhere specified	63,733	82,054	107,018	188,040	287,212
Exports:					
Industrial chemicals:					
Ammonia, anhydrous and chemical-grade aqua (ammonia content)	24,411	14,692	9,513	4,717	3,479
Ammonium nitrate	6,783	2,449	1,554	690	1,663
Fertilizer materials:					
Ammonia, anhydrous and aqua	59,606	93,968	92,904	54,750	71,802
Ammonium nitrate	81,934	36,942	28,324	41,609	23,309
Ammonium phosphates and other nitrogenous phosphatic fertilizer materials	69,071	107,371	77,506	120,520	185,282
Ammonium sulfate	399,675	237,309	144,450	583,418	490,349
Nitrogenous chemical materials, not elsewhere classified	39,399	63,219	18,145	13,524	13,302
Sodium nitrate	1,571	1,040	1,217	954	2,384
Urea	64,574	66,380	72,317	86,742	32,725

[1] This table incorporates some revisions.
[2] Not separately classified prior to Sept. 1, 1963; formerly part of synthetic nitrogenous fertilizer materials.
[3] Ammonium nitrate mixtures containing 20 percent or more nitrogen.
[4] Effective Sept. 1, 1963, classes were combined to become one class; August-December data reported 88,045 short tons, N content 22,011 short tons.
[5] Owing to changes in classification data not strictly comparable.
[6] Data not strictly comparable with other years.

Source: Bureau of the Census

TABLE 4.—*World production and consumption of nitrogen compounds, years ended June 30, 1959–63, by principal countries*

[Thousand short tons of contained nitrogen]

Country	Production					Consumption				
	1958–59	1959–60	1960–61	1961–62	1962–63	1958–59	1959–60	1960–61	1961–62	1962–63
Australia	26	24	23	25	30	39	28	37	44	55
Austria	180	187	187	200	204	55	57	61	67	73
Belgium	336	349	323	304	331	118	114	126	129	143
Brazil	2	13	18	13	24	46	62	66	72	83
British West Indies		6	22	29	29	14	17	18	25	27
Bulgaria	49	69	96	100	119	88	94	115	128	138
Canada	303	355	390	434	519	88	94	123	138	154
Ceylon						26	34	30	34	39
Chile	216	204	160	192	187	23	23	22	25	29
China	231	309	386	408	441	624	661	672	694	838
Cuba		6	6	17	28	22	37	34	77	77
Czechoslovakia	151	159	159	165	177	164	191	197	206	215
Denmark						116	136	141	152	162
Finland	40	41	43	53	49	54	72	73	69	73
France	675	732	844	965	1,010	596	644	748	834	898
Germany:										
East	403	419	408	422	438	320	342	299	325	320
West	1,345	1,404	1,561	1,504	1,617	821	934	908	927	1,108
Greece						78	86	80	91	99
Hungary	40	61	63	75	83	61	66	104	119	121
India	88	105	129	176	234	193	265	277	416	507
Indonesia						31	33	28	116	121
Ireland						23	23	28	33	39
Israel	15	17	22	24	29	17	20	20	22	31
Italy	667	746	819	863	904	412	470	450	487	519
Japan	1,195	1,134	1,290	1,365	1,423	778	849	881	861	903
Korea:										
North	87	88	88	94	99	84	88	99	105	110
Republic of			22	37	44	166	176	193	198	204
Mexico	21	28	35	44	72	132	132	160	171	193
Netherlands	457	481	476	502	531	254	267	263	290	348
Norway	268	293	320	338	355	60	63	58	61	67
Pakistan	11	11	12	22	44	28	31	77	88	99
Peru		4	9	9	17	20	30	33	28	39
Philippines	15	15	15	20	24	47	54	56	80	72
Poland	262	298	311	335	347	281	287	321	335	342
Portugal	46	51	53	73	91	78	83	80	84	88
Rhodesia and Nyasaland, Federation of						24	31	33	39	42
South Africa, Republic of	69	69	88	99	127	83	89	99	105	121
Spain	72	95	129	149	172	308	265	312	369	380
Sweden	37	46	58	66	69	112	131	127	134	143
Switzerland	20	25	35	33	39	20	21	26	29	31
Taiwan	33	43	55	68	77	130	132	122	138	149
U.S.S.R.	882	981	1,146	1,290	1,436	948	1,025	1,067	1,156	1,290
United Arab Republic (Egypt)	37	43	61	117	149	195	160	201	234	248
United Kingdom	524	607	678	700	750	518	632	690	735	758
United States	3,693	3,858	4,034	4,364	4,577	3,759	3,968	4,126	4,558	4,872
Yugoslavia	8	9	9	17	28	86	110	91	91	132
All other countries	19	19	35	54	89	236	375	497	598	680
World total	12,523	13,404	14,618	15,765	17,013	12,376	13,502	14,269	15,717	17,180

Source: Nitrogen. Aikman (London), Ltd., Annual Report on the Nitrogen Industry, No. 15, January 1962, pp. 17–21; No. 27, January 1964, pp. 11–13.

noticeable for anhydrous ammonia and urea, in spite of the great expansion of domestic facilities.

All fertilizer nitrogen compounds and urea enter the United States duty free. The tariff rates on the more important compounds for nonfertilizer use are as follows:

Anhydrous ammonia	Rate Aug. 31, 1963	1.25 cents per pound.
	Statutory	2.50 cents per pound.
Ammonium phosphate	Rate Aug. 31, 1963	0.6 cent per pound.
	Statutory	1.5 cents per pound.
Ammonium sulfate	Rate Aug. 31, 1963	8.5 percent ad valorem
	Statutory	25.0 percent ad valorem.

STRATEGIC CONSIDERATIONS

Nitrogen compounds, including natural nitrates, are not on the Government's list of strategic and critical materials, but they are ingredients of several explosives and thus are important war materials. Nitrogenous fertilizers are essential to maintain and expand the agricultural output of the United States. The capacity of the atmospheric and coke nitrogen industries is sufficient to meet the expected demand in wartime.

GOVERNMENT PROGRAMS

In peacetime, the domestic nitrogen industry operates without any special controls. During wartime or periods when the supply was extremely short, the U.S. Government, the Food and Agriculture Organization of the United Nations, and other organizations have regulated imports and exports, and the U.S. Government has controlled the domestic use of nitrogen compounds.

TABLE 5.—*Yearly price ranges of major nitrogen compounds, per short ton*

Compound	1959	1960	1961	1962	1963
Ammonium nitrate, fertilizer-grade, 33.5 percent N (nitrogen):					
Canadian, carlots, f.o.b. shipping point, bags	$63.00–$68.00	$64.00–$68.00	$64.00–$70.00	$64.00–$70.00	$64.00–$70.00
Domestic, f.o.b. works, bags	63.00– 68.00	64.00– 68.00	64.00– 67.00	64.00–70.00	64.00– 70.00
Ammonium nitrate, domestic with dolomite, 20.5 percent N, bags, carlots, Hopewell, Va	44.50– 48.00	48.00	44.00– 48.00	44.00– 48.00	48.00
Ammonium sulfate, standard granular, bulk, f.o.b. works	32.00	32.00	32.00	28.00– 32.00	28.00– 30.00
Anhydrous ammonia, fertilizer, tanks, works, freight equalized east of Rockies	84.00– 88.00	84.00– 92.00	84.00– 92.00	84.00 –92.00	84.00– 92.00
Cyanamide, fertilizer-mixing grade, 21 percent N, granular, bags, Niagara Falls, Ontario	57.00	57.00	57.00	57.00– 59.00	59.00
Sodium nitrate, domestic, crude, carlots, works, bulk	40.50– 44.00	44.00	44.00	44.00	44.00
Sodium nitrate, imported, crude, carlots, port warehouse, bulk	40.50– 44.00	44.00	44.00	44.00	44.00
Urea:					
Industrial, 46 percent N, bags, carlots, ton lots, f.o.b. plant	[1] 125.00	[1] 98.00–125.00	98.00–100.00	100.00	100.00
Agricultural, 45 percent N, bags, carlots, delivered	[1] 103.00–100.00	[1] 100.00–103.00	[2] 87.25–100.00	[3] 93.25– 96.00	89.00– 96.00

[1] Quoted as "delivered Eastern."
[2] Quoted as "f.o.b. plant."
[3] Quoted as "f.o.b. plant" up to April 9; thereafter quoted "delivered."
Source: Oil, Paint and Drug Reporter.

PRICES

The prices of nitrogen compounds are quoted per short ton of material. In general, prices of major nitrogen compounds were rather steady showing only a slight increase during 1959–63. Urea was an exception, and the drop in prices was due principally to low cost foreign imports.

TAXES

Producers of natural nitrates are granted a depletion allowance of 15 percent on both domestic and foreign production. Numerous domestic producers of atmospheric nitrogen were granted accelerated tax amortization certificates from 1951 through 1956 for expansion and new facilities.

RESEARCH

Since the Atmospheric Products Company first attempted to fix nitrogen in an electric arc furnace in 1902 at Niagara Falls, N.Y., industry in the United States has been conducting research to improve and develop methods of fixing nitrogen. The Chilean Nitrate Educational Bureau, Inc., New York, N.Y., conducts experiments and demonstrations to promote the use of Chilean nitrate.

The Federal Government began active research on nitrogen during World War I, by building two nitrogen-fixation plants at Sheffield, Ala. Plant No. 1 produced ammonia by direct synthesis. Plant No. 2 produced calcium cyanamide.

After World War I, the Government organized the Fixed Nitrogen Research Laboratory under the Department of Agriculture to investigate and improve nitrogen fixation processes. The Plant Industry Station, Department of Agriculture, Beltsville, Md., has taken over this organization, and current activities are concerned mainly with agricultural problems.

The two Government plants at Sheffield, Ala., were closed at the end of World War I and were idle until 1933, when they were turned over to the TVA. Fertilizer research by TVA has been expanded considerably since 1933. Besides the phosphate facilities (see Phosphate Rock Chapter), the Wilson Dam research center includes a synthetic ammonia plant, nitric acid plant, ammonium nitrate plant, and various ammoniators and other fertilizer processing facilities. In addition to basic and pilot-plant research, use tests and cooperative experimental fertilizer applications are being conducted in a number of States.

OUTLOOK

The agricultural demand for nitrogenous fertilizers will continue to increase. The two most important basic factors influencing this increasing use are population growth, anticipated to be about 1.6 percent annually for the next 10 years, and a higher standard of living. The standard of living is directly related to gross national product, which is expected to have a growth rate of 3.8 percent compounded annually for the next 10 to 20 years. In addition, the continued removal of land from agricultural use leads to demands for more fertilizer to increase production per remaining acre.

Domestic production and consumption of high-purity nitrogen was greatly increased during 1959–63 with production in 1963 about 3.7 times that reported for 1959. Demand and production capacities are expected to increase in the next 5 years at a steady but slower pace. It is estimated that the demand for nitrogen by 1970 will have increased to 175 to 200 billion cubic feet.

Further automation of production plants, new and improved methods for manufacturing nitrogen compounds and fertilizers, and better storage and handling equipment will tend to reduce production cost. Also, the trend in the use of higher analysis nitrogen materials will continue, thereby reducing transportation costs per unit of contained nitrogen.

PROBLEMS

The removal of nitrogen compounds from the soil by crops, solution, and erosion presents an obstacle to providing agricultural products needed for the rising standard of living of an ever-growing population.

The fluctuating demand for nitrogenous fertilizers resulting from seasonal requirements, weather, and farm incomes produces problems in production, storage, and transportation. Other problems are encountered when attempting to produce better nitrogenous fertilizers more economically. The industry is concerned with the increasing imports of foreign low-cost ammonia and urea.

New and improved utilization of ammonium nitrate explosives with appropriate safety precautions remains an important problem to the nitrogen industry, as well as to the mining and construction industries.

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OIL SHALE

By L. W. Schramm [1] and J. D. Lankford [1]

VAST deposits of oil shale, a sedimentary rock containing organic matter, comprise the second largest fossil fuel resource in the United States. It is exceeded only by coal and is more plentiful than petroleum and natural gas, which together furnished about three-fourths of the fuel consumed domestically for energy. By far the most important oil-shale deposits in the United States are those of the Green River formation in Colorado, Utah, and Wyoming, which represent a resource of about 2 trillion barrels of oil in place. Liquid fuels of all types, fuel gases, and a wide variety of chemicals can be produced from shale oil, a pyrolysis product obtained by heating oil shale. Interest in the oil-shale deposits of the Rocky Mountain region have risen to a high level since 1963.

The organic material, kerogen, in oil shale is a solid substance which is intimately associated with a mixture of minerals that in most oil shales make up a preponderant share of the rock. Kerogen undergoes a chemical transformation from 800° to 1,000° F to give a major pyrolysis product of oil; secondary products are gas and a carbonaceous residue which remains associated with the inorganic matter. Shale oil obtained in this manner is a mixture of hydrocarbons and hydrocarbon derivatives containing oxygen, nitrogen, and sulfur. By appropriate processing techniques, this oil can be converted to products similar to those from petroleum.

Although oil-shale industries have existed at various times in at least 10 countries, most of them have been discontinued because of competition by lower priced petroleum products. The largest industrial oil-shale operations today are in Estonia and Manchuria.

The economic outlook for commercial production of shale oil in the United States has been improved by technologic advances achieved through research and development during the past two decades. Concurrently, wage increases and the mounting costs of equipment and supplies have tended to hinder shale-oil competition with petroleum. Shale-oil's entry into the domestic market as a supplement to petroleum will be determined by economics—not by a petroleum shortage because petroleum supplies are vast.

Cooperative research and development work by six oil companies and a research foundation is in progress at the Government's oil-shale facility near Rifle, Colo. Recently, the in situ approach to shale-oil extraction has received much attention, although little field testing of this technique has been undertaken. One company has begun work on a project to mine and retort oil shale which is widely reputed to be commercial. The company announced that the plant will be designed to produce about 55,000 barrels per day of crude shale oil.

A major portion of the oil-shale deposits in Colorado, Utah, and Wyoming are on lands in the public domain and are under the jurisdiction of the Department of the Interior. Appropriately, therefore, the Department is engaged in a program for development and implementation of public policies to insure orderly development and conservation of the oil shale and the other natural resources on and beneath the surface of the federally owned oil-shale lands.

BACKGROUND

Commercial production of liquid fuels from oil shales began in France in 1838 and in Scotland in 1850. Subsequently, industries were established and flourished at various times in Australia, Estonia (U.S.S.R.), Sweden, Spain, Manchuria, Kwangtung (China), South Africa, and Germany. Most of these have been discontinued, and today industrial operations

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of appreciable size exist only in Spain, Estonia, Manchuria, and Kwangtung. Much research and development work has been done on Brazilian oil shale in anticipation of future industrial operations.

The Spanish industry is processing about 3,000 tons of oil shale per day for an oil yield of roughly 2,100 barrels. Estonian oil shale (*20*)[2] has a high oil yield, generally about 50 gallons per ton. U.S.S.R. shale-oil production in 1963, mostly in Estonia, has been estimated at 55,000 barrels of oil per day. Part of the Estonian shale is used to produce gas, which is pipelined to Leningrad area.

Manchurian oil-shale operations are thought to be the largest in the world on the basis of tonnage of shale mined and processed. However, the Manchurian shale has a relatively poor oil yield, averaging only about 15 gallons per ton, and oil production is estimated to be between 30,000 and 40,000 barriels per day. Operations in the Chinese Province of Kwangtung are relatively new and are thought to be small.

In Canada and the Eastern United States a small shale-oil industry was operating in 1860 but disappeared when petroleum became plentiful following the Drake discovery oil well in Pennsylvania. Interest in oil shale in the United States was renewed shortly before the 1920's, and numerous experimental projects were undertaken. From 1914 to 1927, a small intermittent, commercial operation was conducted by the Catlin Shale Products Co. near Elko, Nev. However, an oil-shale industry of significant size has never existed in the United States.

Research and development on oil shale in the United States have been conducted sporadically by industry, Government (*2*), universities and others for many years, and there has been sustained interest since World War II.

Intermittently, from 1918 to 1930 the Bureau studied oil-shale retorting, shale-oil refining, and the chemistry of shale oil. During 1944–55, the Bureau conducted mining, retorting, and refining investigations on a pilot plant and demonstration scale near Rifle, Colo. This work was authorized by the Synthetic Liquid Fuels Act (Public Law 290, 78th Cong., April 1944), and subsequent amendments. Laboratory and bench-scale research has been conducted continuously since 1944 at the Bureau's Laramie Petroleum Research Center, Laramie, Wyo., and still is in progress. The Rifle facility, inactive since 1956, was leased to the Colorado School of Mines Research Foundation by the Department of the Interior in 1964 for research and development work. Pilot-plant operations to develop oil-shale-processing technology are being conducted at the Rifle installation under the sponsorship and technical direction of Socony Mobil Oil Co. and Humble Oil & Refining Co. Several other oil companies (Sinclair Research, Inc., Phillips Petroleum Co., Pan American Petroleum Corp., and Continental Oil Co.) are observer participants, and the research and development program is financed by all 6 participating companies.

In 1957, a large experimental retort was erected on Union Oil Co.'s property near Grand Valley, Colo., and was in use for more than a year. The company reported that the retort operated successfully at up to 1,200 tons of shale per day, and that several thousand barrels of crude shale oil from this operation was processed through the gilsonite refining plant near Fruita, Colo. The refined motor fuel products met standard specifications and were sold in regular commercial channels.

In 1963 and 1964 interest increased sharply and recently has risen to a high level. A few manifestations of such interest are articles published recently (*13*, *14*), higher prices for oil-shale lands than those prevailing a few years earlier, expressions by oil companies and others of interest in leasing federally owned oil-shale lands, and an announcement of plans for a commercial venture by Colony Development Co., which is owned by The Oil Shale Corp., Standard Oil Co. of Ohio, and Cleveland Cliffs Iron Co. and will be on oil-shale land owned by the Dow Chemical Co. According to the announcement, the capacity of the installation will be about 55,000 barrels of shale oil per day, and the capital investment is expected to be about $100 million. An initial semiworks unit is scheduled for operation in 1965, and the announced goal for initial production by the commercial plant is 1967.

TECHNOLOGY

The oil-shale technologies developed in various countries of the world (*9–11*, *19*) in general have followed the pattern of mining and crushing the shale, then retorting the crushed shale to obtain crude shale oil, and refining the oil into usable products, mainly liquid fuels. An exception to this general pattern is the Ljungström in situ process, a method of applying electrical heating to oil-shale beds, used in Sweden prior to curtailment of the oil-shale industry there. A unique feature of the Estonian oil-shale industry is that fuel gas is manufactured from some of the oil shale. The characteristics of oil-shale deposits and the

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

properties of oil shales differ greatly from one deposit to another. Because of these and other differences, such as certain economic conditions in one locale versus another, the technology used for one oil-shale deposit often is not suitable for another, or it may require modification before it can be applied successfully to the shales from another deposit. In the United States and some of the other countries having oil-shale resources, the technology derived from research and development has not yet been translated into industrial experience.

Occurrence and Geology

Oil shales are distributed widely throughout the world and occur in sedimentary formations from Cambrian to Recent. They vary greatly in richness, thickness, and rock characteristics. In the United States they occur in at least 30 States (*6*), and, in some instances, in sediments of several different geologic ages within the same State, as shown in table 1. Based on potential oil yield, the most important oil shale occurs in the Green River formation of Eocene (Tertiary) age, which covers approximately 16,500 square miles in adjoining portions of Colorado, Utah, and Wyoming. The other domestic oil shales are of secondary importance as they commonly yield less than 15 gallons of oil per ton and occur in beds less than 25 feet thick.

TABLE 1.—*Oil shales of the United States*

Geologic age	State
Quaternary	Idaho.
Tertiary	Arkansas, California, Colorado, Montana, Nevada, Texas, Utah, Wyoming.
Cretaceous	Colorado, Idaho, Maryland, Montana, South Dakota, Texas.
Triassic	North Carolina, Alaska.
Permian	Idaho, Montana, Ohio, Utah, Wyoming.
Carboniferous and Devonian.	Alabama, Arkansas, Georgia, Illinois, Indiana, Kansas, Kentucky, Maryland, Missouri, Michigan, Montana, New York, Ohio, Oklahoma, Pennsylvania, Tennessee, Texas, Utah, Virginia, West Virginia.
Ordovician	Illinois, Iowa, Nevada, Tennessee, Wisconsin.

The Green River oil shales were formed by the deposition of organic and mineral matter in large shallow lakes that became compact, laminated sediments up to several thousand feet thick. These oil shales or marlstones contain widely varying amounts of organic material and, consequently, yield different amounts of oil by pyrolysis. In Colorado, the Green River formation covers about 2,600 square miles, but the principal oil-shale measures occur in the Parachute Creek member within 1,350 square miles in the Piceance Basin. Although the oil shales in the center of the basin are buried under 1,000 feet or more of overburden, a section nearly 2,000 feet thick has an average assay value of 25 gallons per ton. Sections of this richness become progressively thinner toward the basin margin. Near the outcrop facing the Colorado River, the beds having an average assay of 25 gallons per ton generally are less than 100 feet thick. The Green River formation covers about 4,700 square miles in Utah and 9,200 square miles in Wyoming. The oil-shale deposits in these portions of the formation have not been as thoroughly investigated as those in Colorado. However, present information indicates that, although the deposits in Utah and Wyoming extend over larger areas, generally they are leaner, thinner, and less uniform.

Properties of Oil Shale and Shale Oil

Oil shales consist of solid, largely insoluble organic material intimately associated with a mixture of minerals. Green River oil shale is somewhat resilient, is resistant to fracture, has a Moh's hardness of about 5, and has little porosity or permeability. Detailed analyses giving the compositions, oil yields, and other chemical and physical properties of several grades of the shale have been published (*15*, *18*). Mahogany-zone oil shales have similar characteristics over a wide area; the average composition is shown in table 2.

Kerogen, the organic constituent, is a mixture of high-molecular-weight compounds of carbon, hydrogen, nitrogen, oxygen, and sulfur. According to Himus (*11*), the composition of kerogen in oil shales throughout the world range within the following wide limits: Carbon, 66 to 88 percent; hydrogen, 7.2 to 12.8 percent; nitrogen, 0.1 to 3.1 percent; sulfur, 0.1 to 8.8 percent; and "oxygen plus errors," 0.18 to 24.7 percent. Kerogen is essentially insoluble in alkaline, acidic, and organic solvents. Chloroform or aqueous solutions of chlorohydrate cause it to swell slightly, but only about 10 percent dissolves.

The kerogen in Green River oil shale is believed to be predominantly a heterocyclic material connected to or associated with smaller amounts of hydrocarbon material consisting of straight and branched chain paraffins, cyclic paraffins, and aromatics. A study of low-temperature thermal extracts obtained from this kerogen at 77° to 662° F (25° to 350° C) indicates that it contains approximately 5 to 10 percent straight and branched chain paraffin structures with 25 to 30 carbon atoms, 20 to 25 percent cycloparaffin structures with 3 to 5 rings per molecule, 10 to 15 percent aromatic structures with 3 to 5 rings per molecule, and 45 to 60 percent heterocyclic material containing oxygen, nitrogen, and sulfur.

TABLE 2.—*Composition of oil-shale sections averaging 25 gallons of oil per ton in the Mahogany zone of Colorado and Utah*

	Weight-percent
Organic matter:	
Content of raw shale	13.8
Ultimate composition:	
Carbon	80.5
Hydrogen	10.3
Nitrogen	2.4
Sulfur	1.0
Oxygen	5.8
Total	100.0
Mineral matter:	
Content of raw shale	86.2
Estimated mineral constituents:	
Carbonates, principally dolomite	48
Feldspars	21
Quartz	13
Clays, principally illite	13
Analcite	4
Pyrite	1
Total	100

Shale oils produced from Green River oil shale by the Bureau's Gas Combustion retorting process, the older NTU (Nevada, Texas, Utah) process, and the process of the Union Oil Co. of California, have similar compositions. The gravity of these oils generally ranges from 18° to 21° API. They have a high pour point (about 75° to 90° F), high viscosity (about 300 Saybolt Universal Seconds at 100° F) and contain less than 10 percent naptha. They contain about 0.75 percent sulfur and about 2.0 percent nitrogen. Shale oil is unlike petroleum in that it contains appreciable quantities of nitrogen compounds and rather large quantities of unsaturated compounds. Composition data are fairly extensive on the naphtha fractions (*5*) but are rather meager on higher boiling range fractions.

Mining

A low-cost underground mining method was developed and demonstrated by the Bureau (*6*) at its oil-shale facility near Rifle, Colo., during 1944–56. A "selective mine" was opened first to obtain specific shales from any of the nine beds within the principal oil-shale section, commonly referred to as the Mahogany Zone, for retort testing, and to determine whether theoretical studies on safe roof spans were applicable. A "demonstration mine," sometimes referred to as an underground quarry, then was opened in a 73-foot minable section of the Mahogany Zone to demonstrate the feasibility of a room-and-pillar mining method, to develop and test equipment, and to determine whether low mining costs and high recovery were possible.

Although a mining method having a top heading and two benches was used during the early phase of the mining work, a two-level operation was adopted later—a top heading 39 feet high and a single bench 34 feet high. Head and side space was sufficient to permit the use of large portable diesel and electrically driven mining equipment, thereby obtaining a high output per man-shift. An average of 150 tons per man-shift was achieved for sustained periods during normal operating tests.

Special equipment developed for mining the high faces included drilling jumbos, explosives-loading platforms, scaling rigs, and a mobile compressor and utility station. An electric shovel with a 3-cubic-yard dipper was used to load the broken shale. Diesel-powered end-dump trucks, of 15- to 22-ton capacity, were used for haulage. Room openings and roof-supporting pillars were both 60 feet square. An extraction ratio of 75 percent of the rock in place was attained, leaving supporting pillars which comprised the remaining 25 percent.

Drilling proved to be a major cost item. At first only percussion drills were available, and most of the research on drilling and costs was based on this type of drill. To improve efficiency when drilling vertical holes in the bench mining operation, a hydraulically operated rotary drill mounted on a tractor was developed. For horizontal holes, another rotary drill was developed, but closing of the mine prevented comprehensive testing. A 45-percent semigelatin dynamite was adopted as a standard explosive after much experimental work. Subsequently, new explosives have been developed, and current thinking is that the use of ammonium nitrate explosive mixtures probably would result in lowered blasting costs.

Test-room data indicated a progressive roof deterioration over a period that could result in failure. The minimum roof life was more than 2 years before roof failure would be expected, whereas, in normal retreat-type commercial operations, a unit mine area would be mined out in less than 60 days and then closed to entry. This period of open entry, which is much shorter than 2 years, would leave a substantial margin of safety for a retreat-type mining operation.

In the early 1950's, cost estimates based on data developed at the demonstration mine were made by the Bureau and industry groups in cooperative studies. The estimates ranged from 48 to 56 cents per ton for mining and crushing oil shale and conveying the crushed material to retort stockpiles. These estimates included labor, supplies, depreciation, local taxes and administrative overhead, but not depletion, interest on investment, expenditures for offsite facilities or cost of oil-shale land. These figures

pertained only to costs and therefore did not include profit or income taxes. During the years since estimates were made, labor rates and equipment prices have increased, but it is believed that the escalating effect of these increases on oil-shale mining cost has been largely offset by technologic advances. Changing to rotary drilling in the mine heading as well as in benching; blasting with a more economical explosive, such as an ammonium nitrate-oil mixture; use of better drilling, haulage, and loading equipment; and other improvements based on recent advances in quarry and open-pit mining engineering can be expected to lower costs substantially. Accordingly, mining oil shale on a large scale probably still could be achieved at close to 50 cents per ton.

The optimum size of a single room-and-pillar mine currently is envisioned at about 30,000 tons per day. Mining a continuous section 100 feet thick at this rate, with 75 percent extraction, would deplete an area of about 1,050 acres in 20 years. This amount of oil shale would produce almost 120 million barrels of oil if the average assay were 25 gallons per ton and if overall retorting efficiency were 90 percent of assay.

The room-and-pillar mining method may be adaptable to shales other than those of the Mahogany Zone and to areas far separated from an outcrop by gaining entry to the shale through vertical shafts. Open-pit mining probably will be practical in some areas where the ratio of overburden to shale is not excessive.

Crushing

The Bureau has obtained substantial data on crushing Colorado oil shale using different types of equipment including jaw, gyratory, impact, and roll crushers. Experience and data were accumulated on two- and three-stage size reduction throughout the testing and development program conducted at its oil-shale project near Rifle, Colo. In addition, data were derived from a number of crushing tests of short duration which were conducted cooperatively between the Bureau and several industrial machinery companies. As a result of these studies and operating experience, valuable information was acquired and relationships were derived on oil-shale properties as functions of type of crushing equipment and retorting processes. For example, a significant property of oil shale from the richer strata of the Mahogany Zone is that it is tough and resilient and tends to form slabs, which produce operating troubles especially when crushed in a jaw-type crusher. For some processes, such as the Gas Combustion (*3*) retort pioneered by the Bureau, a large amount of very small particles is not desirable and crushing equipment for preparing its oil-shale feed should be chosen that minimizes fines production.

Although the crushing step is not considered as a critical problem, a number of factors will be important in designing commercial crushing plants and in selecting the most suitable equipment. The cost of crushing is a relatively small part of the overall cost of producing liquid fuels from oil shale. In 1955, the cost of reducing mine-run shale with a maximum particle size of 60 inches to minus 3-inch particles was estimated to be about 15 cents per ton.

Retorting

Heating is the only practical means known to produce shale oil from oil shale. From 800° to 1,000° F, the organic material, kerogen, which is a solid substance, undergoes a chemical transformation by pyrolysis, in effect a thermal cracking. The major pyrolysis product is oil; secondary products are gas and a carbonaceous residue which remains on the retorted shale.

Three retorting processes designed for processing the oil shales of Colorado, Utah, and Wyoming have progressed through various stages of pilot-plant development, and offer promise for commercial application. One of the three processes was developed by the Bureau, another by the Union Oil Co. of California, and the other by The Oil Shale Corp. (now a part owner of Colony Development Co.); the processes are known as Gas Combustion, Union, and TOSCO, respectively. Another, known as the Entrained Solids retorting process (*16*), has been developed by the Bureau through laboratory and small pilot-plant experimentation, and shows considerable promise of finding commercial application in processing oil-shale fines (particles smaller than about one-fourth inch) that probably will be removed by screening from the feed to Gas Combustion and perhaps other retorts. In situ retorting may become an important shale-oil extraction method, but the technology is still in an early stage of development.

In the Bureau Gas Combustion process, a bed of oil-shale particles, ranging in size from about one-fourth inch to 3 or 4 inches, moves down through a vertical retorting vessel while gas flows up through the bed. Air mixed with gas is injected into the central portion of the retort, and combustion of the gas provides much of the heat for retorting. Some of the residual carbon in the retorted shale burns also, providing additional heat. Oil vapors from the retorting zone condense as small droplets to form a mist in the upper portion of the moving bed of particles. The mist is carried out of the

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retort by the effluent gas stream, and is then separated from the gas by suitable agglomerating equipment such as centrifugal separators. Part of the gas is recirculated through the retort to provide the major fuel for the Gas Combustion process. The process was studied by the Bureau in three sizes of pilot plants, the largest of which was operated at about 200 tons of shale per day. Further development has been initiated at Rifle under the previously described leasing arrangement with private organizations.

The Union Oil Co. process uses a vertical, continuous, retort which is underfed with shale and has a countercurrent gas flow from an internal-combustion zone. Crushed oil shale, with pieces ranging up to the size of a double fist, is forced upward from the bottom of the retorting vessel by means of a ramlike piston that serves as a "rock pump." Air and combustion gases flow downward through the shale bed. As the shale moves upward, it passes progressively through a zone where downward flowing gases and products are cooled and shale oil is condensed; a retorting zone, where gases from combustion heat the shale to pyrolysis temperature; a combustion zone, where combustibles and residual carbon on the retorted shale are burned; and finally a cooling zone, where the incoming air absorbs some of the heat content of the retorted shale. The hot spent shale spills over the top of the retort into a chute and passes from the system.

In the TOSCO retorting process, oil shale, crushed much finer than the feed to the Union and Gas Combustion retorts, is introduced continuously, along with hot ceramic balls, into a horizontal, kiln-type, rotating drum. The shale is heated to retorting temperature (about 900° F) through direct contact with the heat-carrying balls. Oil vapors and product gas released by the pyrolysis are withdrawn from the rotating drum and enter a recovery system, which includes a "soaking" drum where additional cracking occurs as well as condensing and collecting equipment. The ceramic balls leave the drum and are reheated after a part of their heat content is given to the shale. The retorted shale is sent to equipment where the residual carbon is burned off, and the heat so generated is used to reheat the ceramic balls. This process is a greatly improved evolvement of the Aspeco retorting system, a process that was conceived in Sweden by Olaf Aspegren. Under a contract with The Oil Shale Corp., the Denver Research Institute assisted in the development of the TOSCO process in a 25-ton-per-day pilot plant.

Many retorting processes have been proposed, but they either have been rejected because they were inoperable or were lacking in one or more of the essential characteristics for successful application to the oil shales of Colorado, Utah, and Wyoming—or they have faded into the background because research and development work on them has not been pursued far enough to demonstrate their merit. The Socony Vacuum Oil Co. (now Socony Mobil Oil Co.) studied the application of their patented Thermofor catalytic cracking equipment to oil-shale retorting. Standard Oil Development Co. (now Esso Research & Engineering Co.) conducted retorting tests in a modified two-vessel fluid catalytic cracking pilot plant. The Bureau experimented with several processes (*1*), namely, Hayes, NTU, Pumpherston, Royster, Gas Flow, Counterflow, and Thermal-Solution, but discontinued work on these in favor of the Gas Combustion process.

The most recent work on oil-shale utilization involves studies by oil companies of in situ retorting using interconnections between wells in shale formations resulting from oil-well fracturing techniques. Such interconnected wells would serve as input and producing wells for underground combustion which would provide heat to retort the oil shale underground. Shale oil then would be liberated and withdrawn from one of the wells.

Sinclair Research, Inc., a subsidiary of Sinclair Oil Corp., initiated work in 1964 on an in situ oil-shale retorting test in the Piceance Creek area in Rio Blanco County, Colo., where the oil-shale beds are hundreds of feet thick. Sinclair operated a pilot in situ project (*8*) in the early 1950's at Haystack Mountain, near Debeque, Colo., where the oil-shale beds are thinner and relatively near outcrop areas. Other oil companies and the Bureau have conducted laboratory and bench-scale work to obtain data for application in the development of in situ retorting methods and techniques, and several companies have conducted field investigations of a preliminary character.

Refining

Shale-oil refining research and process development in the United States have been focused to a large extent on adapting petroleum refining techniques to shale-oil processing and to a limited extent on developing new processes especially suited to the characteristics of shale oil. This approach was taken in the interest of utilizing existing oil industry methods and equipment and thereby achieving a flexibility that will permit movement of shale oil products when they become available into regular petroleum channels.

Shale oil produced in retorts designed to obtain a high-percentage yield of oil contains only

a small quantity of distillate in the gasoline-boiling range. Both straight-run distillate and residual fuel oils can be prepared directly from crude shale oil, but the distillate fuels usually require treatment to meet specifications.

Gasoline and diesel fuel were obtained by thermal cracking and low-temperature chemical treatment in the Bureau's experimental refinery (*12*) at Rifle, Colo. The shale gasoline met the specifications then in effect for regular-grade gasoline and was burned in automobiles used on the project. Shale diesel fuel produced in the experimental refinery was tested in several types of diesel-powered equipment and in railroad locomotives, and it was regularly used in the diesel equipment on the project. Performance was satisfactory and comparable to that obtained with regular commercial diesel fuel. In a commercial shale-oil refinery, tar bases and tar acids removed from the lighter distillate fractions by washing with sulfuric acid and caustic solutions, as was done at Rifle, would be produced in rather large quantities. These tar acids and bases would have byproduct value.

Hydrogenation, re-forming, desulfurization and nitrogen removal, catalytic cracking of reformates, and other modern refining processes have been studied on a laboratory scale at the Bureau's research facility in Laramie, Wyo. (*7*).

Crude shale oil contains waxes and high-viscosity materials which cause it to have a high pour point (90° F); therefore, it is not pumpable at ambient temperatures. Vis-breaking, a mild thermal cracking, or coking, a more severe thermal cracking, produces shale oil suitable for pipeline transportation. Recycle cracking of crude shale oil produced a yield of over 50 percent gasoline-boiling-range naptha in the experimental refinery. Thermally cracking crude shale oil to yield coke and a coker distillate boiling lower than the original crude may be advantageous as feedstock preparation for subsequent refining in operations such as hydrogenation, catalytic cracking, desulfurization and nitrogen removal. Re-forming the gasoline fraction by either thermal or catalytic processes improves its octane rating. Cracking of crude shale oil or its high-boiling fractions at elevated temperatures or in the vapor phase results in highly aromatic products. This aromatic oil may be hydrogenerated readily to premium-grade gasoline or aromatic chemicals.

Hydrogenation is an effective means of removing sulfur, nitrogen, and oxygen from shale oil and of stabilizing the more reactive unsaturated components, thereby reducing their gum- and color-forming tendencies. Excellent yields of high-quality jet, diesel, and distillate fuels can be produced by this method of refining. Hydrogenated oils also are satisfactory charging stocks for catalytic cracking and reforming processes and may be suitable for use in manufacturing lubricants. Laboratory investigations have demonstrated that without any treatment such as hydrogenation to remove nitrogen, shale-oil stocks are unsatisfactory feed materials for catalytic cracking processes currently used in the petroleum refining industry because nitrogen compounds in shale oil "poison" (have a deactivating effect on) cracking catalysts.

Several overall shale-oil refining procedures made up of various combinations of unit operations such as those mentioned have been evaluated and could be used to produce a full range of liquid fuels.

Waxes having properties similar to petroleum waxes can be separated from shale-oil fractions by conventional dewaxing processes. Shale-oil asphalts and road oils were used to surface roads at the Bureau's facility near Rifle, Colo. Shale-oil pitch was used experimentally and found satisfactory as a blending agent with coal at a Utah steel mill to produce metallurgical-grade coke. Shale-oil coke was found to offer promise for use in blast furnaces and in the manufacture of electrodes and carbon brushes.

USES

Shale oil will be utilized in much the same manner as petroleum and will become a supplemental source of liquid fuels. Gasoline, jet fuel, diesel fuel, and fuel oils are expected to be the major shale-oil products. Properties of these products obtained from shale oil closely resemble those of their petroleum counterparts and will meet the same specifications. Shale-oil fuels are expected to merge into the use pattern of petroleum fuels (see Petroleum chapter of this bulletin). Chemicals similar to many of the petrochemicals manufactured from petroleum, particularly olefinic, aliphatic, and aromatic hydrocarbons such as naphthalene, also may be produced from shale oil. Some inorganics such as sulfur and ammonia also are expected to be byproducts of an oil-shale industry. However, shale oil probably will not be a significant source of lubricants, inasmuch as petroleum stocks better suited for this purpose are plentiful and require less processing.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Because shale oil differs in composition from most natural crude oils in some respects, its refining may result in byproducts not commonly obtained from petroleum, at least not in as large quantities. Among these are chemicals such as tar acids and tar bases, which normally are con-

sidered as coal tar derivatives, but also are obtainable from some shale-oil distillates under particular types of treatment.

Byproducts may be produced in conjunction with oil-shale retorting plants as well as shale-oil refineries. Large volumes of low Btu gas will be obtained from internal-combustion retorts. Other retorts will produce gases rich in hydrogen, hydrocarbon gases, carbon dioxide, and hydrogen sulfide. Decarbonization of the heavy oils to produce the desired distillate materials will result in large amounts of coke if coking is utilized as an initial processing step. Coke would not be a major product if the crude were hydrogenated. Among the hydrocarbon gases are ethylene, propylene, and other olefins of interest to the chemical industry. All retorting processes will discharge spent shale. Although no large-tonnage uses for this inorganic material are foreseen, it may find local uses in special situations such as for low-cost fill. However, the problems and expense that may be involved in disposing of spent shale in large quantities are expected to more than outweigh the credit that may accrue because of such limited uses.

RESOURCES

Estimates of oil in place in the principal known oil-shale deposits of the world are given in table 3. Only a portion of these shale-oil resources can be regarded as likely to be economically recoverable in the near future using present technology. Some of the beds are too lean to be of commercial interest any time soon, and the application of mining methods presently considered suitable would not remove all the oil-shale from the deposits. At the same time it should be remembered that the presently known resources represent only part of the world's total shale-oil potential. Investigations of some of the known deposits have been limited, and additional deposits may be discovered in the future. However, it is believed that the estimates shown in table 3 portray the order of magnitude of shale-oil potentials of the known deposits in the countries listed, with the possible exception of Canada. Whereas only the Albert shale deposits in New Brunswick are included in the estimate, there are reports in the literature of several other deposits in Canada.

The oil shales of the Green River formation in Colorado, Utah, and Wyoming are by far the most important deposits in the United States. Some of the other States have substantial shale-oil resources, but the deposits usually are relatively low grade, are not as well defined nor as amenable to low-cost mining and processing, and therefore are less attractive economically than the Rocky Mountain deposits as a shale-oil resource potential.

TABLE 3.—*Estimates of the major known shale-oil resources of the world in oil shales assaying 10 gallons per ton or more* [1] [2]

Country or area	Oil in place, million 42-gallon barrels
Argentina	400
Australia, including Tasmania	270
Balkans and other Central Europe [3]	340
Brazil	800,000
Burma	2,000
Canada (Albert shale in New Brunswick) [4]	50,000
Chile	20
China:	
Fushun, Manchuria	2,100
Other deposits	26,000
England	1,000
France	425
Germany, West	2,000
Israel	20
Jordan	45
Sicily	35,000
Luxembourg	700
New Zealand	560
Republic of the Congo	100,000
Republic of South Africa	130
Scotland	580
Spain	280
Sweden	2,500
Thailand	800
United States:	
Colorado, Utah, and Wyoming	2,000,000
Central and Eastern States	200,000
U.S.S.R.:	
Estonia and adjacent Leningrad Area	22,000
Other European U.S.S.R.	13,000
Siberia	80,000
Total [5]	3,340,170

[1] Estimates are based on oil-shale formations thick enough to be considered minable in the future; most of the shale-oil resources are in thick oil-shale sequences.

[2] Based on a comprehensive treatment of the subject by Donald C. Duncan and Vernon E. Swanson of the Geological Survey in "Organic-Rich Shale," prepared as a chapter of a treatise on world energy resources. The manuscript of the shale chapter was in the review process preparatory to publication at the time this table was prepared. Many references to published information on the subject are contained in the manuscript.

[3] Countries included are Bulgaria, Yugoslavia, Albania, Greece, Czechoslovakia, Austria, and Switzerland.

[4] This is an order-of-magnitude estimate for the richer oil-shale sequences in the Albert Formation. Deposits of oil shale also are known to exist in Newfoundland, Nova Scotia, Ontario, Quebec, Saskatchewan, and Manitoba.

[5] Rounded total, 3.3 trillion barrels; energy equivalent, 19×10^{18} Btu. Nominally, shale oil of average composition is assumed to have an energy equivalent of 5.9×10^6 Btu per barrel. The gross heating value of crude shale oil produced by the modified Fischer assay retort from a composite oil-shale sample representative of the Mahogany Zone in Colorado is 18,510 Btu per lb, and the specific gravity of this crude shale oil is 0.916 at 60°/60° F (Bureau of Mines Report of Investigations 4825, 1951, p. 25). Accordingly, the gross heating value of this particular shale oil is 5.93×10^6 Btu per barrel.

Source: Geological Survey.

Analyses have been made by the Bureau (*17*) on more than 90,000 core and drill-cutting samples of the oil-shale deposits in the Green River formation. The samples were provided for the most part by companies engaged in evaluating oil-shale properties and drilling for oil and gas. The data provided by these assays are the principal source of oil-yield information used by the Geological Survey and others for resource evaluations. In Colorado, Utah, and Wyoming the shale-oil equivalent of beds richer than 10 gallons per ton and at least 15 feet thick is estimated at about 2 trillion barrels. Accord-

ing to the Geological Survey, the oil potential of the principal oil-shale deposits in Colorado's Piceance Basin includes about 500 billion barrels in shale yielding more than 25 gallons per ton and about 800 billion barrels in shale yielding between 10 and 25 gallons, or a total of 1.3 trillion barrels in combined high- and low-grade oil shale.

In Utah and Wyoming, estimates of oil in place in shale formations at least 15 feet thick assaying 25 gallons per ton or more are 120 billion barrels and 43 billion barrels, respectively. Utah's oil shales in beds at least 15 feet thick that will yield an average of 15 gallons per ton are estimated to represent about 320 billion barrels. In Wyoming, the shale oil in beds richer than 10 gallons per ton is estimated at 370 billion barrels.

The percentage of in-place oil that may be recovered economically depends principally on such major factors as extraction ratio achieved in mining, amount of fines discarded, if any, and retorting efficiency. In areas amenable to mining by underground methods developed by the Bureau at Rifle during 1944–55, it is estimated that about two-thirds of the in-place oil could be recovered using those mining and processing techniques that were demonstrated there.

GOVERMENT PROGRAMS

A major portion of the oil-shale deposits in Colorado, Utah, and Wyoming are on lands in the public domain which are under the jurisdiction of the Department of the Interior. Jurisdictional responsibilities apply not only to the land but also to the minerals and other natural resources on and beneath the surface of the land.

Prior to 1920, disposition of publicly held oil-shale lands had been governed by mining laws, and many claims had been filed under the U.S. mining law of May 10, 1872, but had not been brought to patent. Under the Mineral Leasing Act of February 25, 1920, oil-shale deposits in the public domain were made subject to leasing, rather than to location as mineral placer claims as formerly, with the exception that valid oil-shale mining claims existing on that date could legally be brought to patent. The federally owned oil-shale deposits and the lands containing such deposits were withdrawn from lease or other disposition by Executive Order 5327 of April 5, 1930, to allow clarification of the status of land ownership and title. This order has not been lifted since then, and it has not been possible to lease Federal oil-shale deposits, although later the order was modified to permit petroleum and natural gas operations and exploitation of sodium minerals such as the trona deposits in Wyoming near the town of Green River.

As a guarantee of oil for the Navy in future emergencies, the Government has segregated and held apart for such purpose certain sections of the public domain containing oil shale. Approximately 62 square miles of oil-shale land on the public domain in Colorado (Shale Reserve No. 1) and approximately 150 square miles in Utah (Shale Reserve No. 2) were reserved for the Navy by two Executive orders in 1916 and subsequent modifying orders. By an Executive order in 1924, approximately 35 square miles of land in Colorado (Shale Reserve No. 3), adjacent to the naval reserve that had been established earlier, were reserved primarily for the purpose of providing sites for plants to process naval-reserve oil shale and space for disposal of the resulting spent shale.

The Department is engaged in a program (*4*) for the development and implementation of public policies to insure orderly development and conservation of the federally owned oil-shale deposits, and to foster the most beneficial use of all oil-shale lands. A group of distinguished citizens from outside the Government, known as the Oil-Shale Advisory Board, have been appointed by the Secretary of the Interior to assist the Department in developing background and solutions to the many-faceted oil-shale policy problems. Implementation of sound policies will greatly aid oil shale's contribution to the Nation's long-term economic growth, add substantially to the national security, and permit wise use of the land, mineral, and water resources.

TAXES

Under present tax laws, a depletion allowance of 15 percent of the value of the oil-shale rock as mined can be deducted from the taxable income of a commercial oil shale operator in figuring income tax liability (provided that amount does not exceed 50 percent of taxable income computed without allowance for depletion). Oil shale, as petroleum and all minerals, is a natural resource which is entitled to a depletion allowance. The depletion-allowance provisions of Federal tax laws reflect a recognition of the wasting-asset nature of the extractive mineral industries. Allowable percentage depletion rates range from 5 to 27.5 percent.

Imports of petroleum and its products are likely to have an economic relationship to a shale-oil industry analogous to their relationship to the domestic petroleum industry. Accordingly, in the future, Government policies regarding petroleum imports may be expected

to have a significant bearing on a shale-oil industry.

RESEARCH

Methods, procedures, and equipment for mining oil shale, extracting shale oil, and processing the oil have been developed to varying degrees of refinement in many countries. The existing oil-shale technologies in various parts of the world are products of research and development, combined in most instances with industrial oil-shale operating experience. Patents relative to oil-shale and shale-oil processing number over 2,000, and new ones continue to be issued.

In the United States, there has been substantial oil-shale research and development, most of which has occurred during the past 20 years. Oil companies and other industrial firms, the Bureau of Mines, educational institutions, and individuals have engaged in this work. The overall objective of most such efforts has been to effect technological improvements that would lower the cost of producing liquid fuels from oil shale.

The in situ approach to shale-oil extraction, now receiving much attention, offers promise at least in concept of becoming an extremely valuable tool for extracting oil from the oil shales of the United States. It may prove to be applicable to deep-lying oil-shale beds and deposits that are hundreds of feet thick, such as those in the center of the Piceance Basin. Mining of oil shale from such deposits probably would be expensive and difficult. In situ retorting also may be found applicable to oil-shale beds that are too thin or too lean to be attractive for mining. However, the technology is in an early stage of development, and time and effort will be required to establish the feasibility of the in situ method and to define its capabilities and limitations.

The oil-shale program at the Bureau includes both basic and applied types of research. These investigations may be grouped principally in the following broad categories: (1) studies of the structure and composition of kerogen and its chemical and physical properties; (2) developing information on the characteristics of the Nation's oil-shale deposits, with emphasis on those of Colorado, Utah, and Wyoming; (3) obtaining scientific and engineering information needed to solve problems encountered in the development of retorting and refining processes; (4) laboratory studies that provide technical information and data which may be used in developing in situ oil-shale retorting methods; (5) shale-oil processing studies, especially the application of hydrogenation techniques in combination with other petroleum refining processes; and (6) evaluation of shale oil as a source of chemical products.

Some preliminary studies have been made jointly by the Bureau and the Atomic Energy Commission to obtain information needed in the planning of experiments tentatively contemplated and designed to assess the possibilities of using nuclear explosives in connection with in situ oil-shale operations. As yet no field experiments involving nuclear devices have been initiated. Part of one concept of using a nuclear explosive would be to create an underground cavity by a nuclear device. Subsequently, the cavity would become filled with broken rock from caving, and this rock-filled cavity then might be retorted in place, much as in a batch-type conventional retort such as the NTU. The oil retorted from the shale then could be withdrawn from the base of the cavern.

A continuing growth of the fund of basic scientific oil-shale knowledge can be expected to lead to advances in mining and processing techniques and to new and improved products. This knowledge embraces such aspects as constitution and structure as well as the chemical and physical properties of oil shale and its organic and inorganic constituents. The chemical reactions involved in the conversion of kerogen to shale oil and refined products also constitute an important aspect of this branch of scientific knowledge.

OUTLOOK

The oil shales in the Green River formation of Colorado, Utah, and Wyoming, the world's largest concentration of hydrocarbons, someday are expected to be a source of shale oil that will constitute an important supplement to petroleum. However, the time of entry of shale oil into the fuels market and the growth rate of future shale-oil production are conjectural.

Commercial shale-oil production in the United States can be expected whenever there is sufficient economic incentive. Before large amounts of capital are committed for this purpose, the public and industry must have assurance that shale-oil products can supply some of the demand for liquid fuels as well and as profitably as counterpart fuels can be produced from domestic petroleum or other fossil-fuel resources. Shale-oil production is not expected to be brought about by shortages in other forms of energy, but by the respective economics. Do-

mestic petroleum reserves alone are regarded as adequate for the foreseeable future.

The current economic position of shale oil is only vaguely defined; however, there is a general belief that oil from oil shale would not be much more costly than domestic petroleum. The view that shale oil can enter the domestic market before many years is reflected by the current high level of activity and interest in oil shale. Further research and development are needed to fill gaps in present technical knowledge and to lower mining and processing costs. Such research and development may take several years. Furthermore, approximately 3 years will be required for design and construction of commercial plants after a decision is made to proceed with commercial development.

It is unlikely that hydrocarbon resources other than petroleum will retard oil-shale development appreciably. Some of the oil to be produced from Canadian tar sands may be marketed in the north-central United States. However, if the governments of the Canadian Provinces continue to follow their present policy of limiting production of oil from the tar sand deposits, the quantities of oil from this source entering the United States during the relatively near future will be small. Also, it is believed that California rather than the Northern States will provide the first large market for shale oil, though eventually the north and eastern industrial sections of the Nation may provide the largest market.

Tar-sand deposits in the United States are smaller than those in Canada and have received comparatively little attention, although experimental operations of short duration in the past have been conducted from time to time, especially on deposits in Utah and California. However, interest has been growing in shallow tar sands, or heavy-oil deposits, in Oklahoma, Kansas, and Missouri, where such resources may be quite large although not well defined. Oil from these deposits is not expected to affect the potentially large west coast shale-oil market initially.

The anticipated increase in demand for petroleum products can be expected to favor expansion of shale-oil production, once it has started. Between now and the end of the century, the demand for liquid fuels is expected to rise to about three times its current level in the United States and to increase still more rapidly in the rest of the free world.

Eventually, oil shales may be used to provide gaseous as well as liquid fuels. However, economic considerations indicate that commercial production of fuel gas from oil shale to supplement natural gas is much farther in the future than production of shale oil to supplement petroleum.

PROBLEMS

Aside from the need for additional knowledge in resources and technology, some of the principal problem areas associated with the Rocky Mountain oil-shale deposits are those involving economic and legal matters and questions of public policy. These problem areas include a need for measures to insure conservation and multiple use of the several natural resources in the geographic areas in which the oil-shale deposits lie, anticipated economic effects of industrial development, and shale oil's competitive position with respect to other fuels.

Information is lacking and questions have been raised on the validity of many of the oil-shale mining claims that were filed prior to enactment of the Mineral Leasing Act of February 1920 but not patented. The Department of the Interior's authority to lease a large share of the oil-shale lands on the public domain will not be clear until the validity and various legal and title questions on the multitude of unpatented mining claims have been settled.

In the field of resources, problems in the realm of conservation from a technical standpoint are among the most difficult. Many of the oil-shale lands contain additional known or potential resources, both mineral and nonmineral, and the present and future values of these also must be considered. Among these resources are the land itself, as well as the subsurface oil and gas, sodium minerals, and ground water. Included to an increasing extent as the Nation's population grows are a number of items having esthetic and intangible values upon which it is difficult to place monetary worth such as freedom from air pollution, retention of outdoor recreation areas, and prevention of undue disruption of wildlife habitat. Strip mining could spoil the land surface for other uses. High-grading and other unwise mining and plant practices could waste large amounts of oil shale, result in enormous spoil piles, and create problems in stream and air pollution. In situ mining could adversely affect the extraction of other minerals, and caving of underground mines could affect the surface and impair recovery of sodium minerals that in some places lie above the oil-shale deposits.

Variation in the thickness and richness of the deposits, which relate to the expense of mining

or in situ processing at various locations, is a matter for consideration in the formulation of policy on leasing. Under the Mineral Leasing Act of 1920, a tract up to 5,120 acres, regardless of location, could be leased if the Executive withdrawal order of 1930, mentioned earlier, were not in effect. However, the oil shale beneath an acre of ground in the central portion of the Piceance Basin contains the kerogen equivalent of more than 10 times as much oil as that of an acre toward the basin margin.

The cost per barrel of producing shale oil by mining and retorting will be substantially lower for an operation on the order of 50,000 barrels per day than it would for a small operation such as 5,000 barrels a day. Accordingly, it is doubtful that small-scale operations would be economic or practical. The capital requirement for an economic-scale shale-oil production facility in the 50,000-barrel-per-day range would be as great as $3,000 per barrel of daily capacity, which is out of reach of most small operators. The exact amount involved would vary substantially depending on land costs, type of plant built, related facilities, and degree of processing beyond the point of producing crude pipeline oil.

The great thickness of some of the deposits and interbedding of high- and low-grade layers of oil shale will make these deposits difficult to mine underground in a way that will yield full recovery. In the mineral industries there often has been a tendency during the early stages of developing an orebody to focus mining plans on high-grade seams; selective extraction of rich beds of oil shale may jeopardize later recovery of associated lower grade beds.

Efficient and economic recovery of shale oil from the thick but deeply buried deposits in the central portion of the Piceance Basin will require development of in situ processing technology or of suitable mining methods. Such mining methods must be low cost and must be applicable to deposits some of which are up to 2,000 feet thick and overlain in some areas by more than 1,000 feet of overburden.

Ascertaining an optimum rate at which industrial oil-shale development should proceed will involve factors that vary widely in scope and include local, national, and international considerations. Among these will be the effects of future shale-oil production rate on the orderliness of commercial oil-shale development, the economics of the oil-shale industry, the economics of the petroleum and natural gas industries, the local and national economies, and the position of the U.S. energy complex in the economies of nations around the world. Tax treatment, leasing regulations, and other measures are all policy considerations that may bear on acceleration, retardation, or stabilization of the rate of industrial oil-shale development.

The supply of water in the Rocky Mountain States, a semiarid region, is limited. Eventually, lack of water in sufficient quantities easily could prove to be a limiting factor in the extent of oil-shale development and in the attainable production capacity. Significant quantities of water will be essential for the oil-shale mines and extraction plants even if the bulk of the shale is processed by retorts which have no need for cooling water and even if most of the refining is done out of the area, such as on the west coast or other points of end use. In addition, large amounts of water will be needed by the cities and towns that will grow in the vicinities of the future mines and retorting plants and by satellite industries. Such water needs are expected to be larger than shale plant industrial uses.

Additional work on the two-level room-and-pillar mining system, or an alternate method, is needed to assure adequate safety in future underground oil-shale mines. Rotary drilling of horizontal blast holes, initiated during the latter stages of the Bureau's operations at Rifle, requires further development and testing to provide the techniques, experience, and data needed for design of commercial rotary drilling machines. Likewise, studies are needed to investigate the cost-reduction potential of new explosives such as ammonium nitrate-oil mixtures. Earlier studies showed dynamite to be the largest single supply expense for mining.

Further development of retorting processes, including the operation of prototype plants, can provide process and engineering improvements leading to greater throughput, better efficiency, and reduced overall costs. The benefits of this work would be magnified in proportion to the growth of the future industry. Along this line, development work on retorting has been renewed at the Rifle facility by industry under the lease arrangement mentioned earlier. The results of this work will be published by the Bureau later under the terms of the lease agreement. In the meantime, the Bureau has engineers stationed at Rifle to observe all operations and obtain all testing and operating data.

Further assessment of the Green River deposits is needed, especially in Wyoming and Utah, where samples to date have been sparse. Oil-shale deposits other than those of the Green River formation, in other States, also should be appraised more fully as only meager data now are available.

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PEAT

By Eugene T. Sheridan [1]

PEAT is partially decomposed vegetable matter that has accumulated under water or in a water-saturated environment. It is the initial stage in the transformation of plant materials into coal. When peat is buried beneath deposits of clay, sand, limestone, or other sedimentary beds and subjected to heat and pressure, usually by movements of the earth's crust, its physical and chemical properties are changed, and it becomes coal. The nature of the original vegetation, the conditions of its deposition as peat, and the subsequent geologic history all influence the characteristics of the resultant coal.

There are known peat deposits in at least 35 States, and total U.S. reserves have been estimated at approximately 14 billion tons. The bulk of the reserves are in 4 States—Florida, Michigan, Minnesota, and Wisconsin. Approximately one-half of the total, however, is in Minnesota.

Although used for fuel in other countries, peat cannot compete in U.S. fuel markets but is produced for use in agriculture and horticulture, principally as an amendment for soil improvement.

Markets for peat have increased steadily in the United States in recent years and, within the past decade, domestic production has more than doubled, reaching nearly 600,000 tons in 1963. In addition, 261,000 tons of peat, most of which was used for soil improvement, was imported.

The domestic industry in 1963 consisted of 113 active operations in 23 States. The principal producing States were Michigan, Indiana, Pennsylvania, California, and Washington which, collectively, produced about three-fourths of the total output.

World production of peat in 1963 was estimated at 170 million short tons, of which an estimated 60 percent was used for agricultural purposes and the remainder for fuel. The U.S.S.R. was the leading producer with an estimated 95 percent of the world output.

BACKGROUND

The earliest recorded use of peat for fuel dates back to the dawn of history. The Romans mentioned its use at the time of their conquest of northern and western Europe. They observed that the people of those regions dug soil from the marshlands with their hands, after which they dried and burned it to cook their food and to keep themselves warm. Thus, for centuries, peat has been burned for fuel, particularly in Ireland. In more recent times, peat has been used as fuel for heating and cooking in other northern European countries that, lacking deposits of coal, used wood as a domestic fuel until the forests were cleared for farming. Within the past few decades, peat has been developed as an industrial fuel in Europe, and a number of countries, particularly the U.S.S.R. and Ireland, now burn large quantities of peat to generate electric power.

Small quantities of peat were used for fuel in some areas in the United States almost continuously from the time of settlement until the beginning of the 19th century. But as transportation systems were improved, coal came into general use, and the use of peat for fuel was discontinued. No peat has been sold commercially for fuel in the United States for several decades.

The advantages of using peat in certain agricultural applications were recognized in the 20th century, and a peat industry engaged in producing peat for agricultural and horticultural purposes began to emerge around 1904. At this time there were about a dozen companies producing a few thousand tons of peat annually.

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Since then the industry has expanded greatly, and in 1963 there were 113 active operations that produced more than one-half million tons of peat.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

There were 113 active peat operations in 23 States in 1963. Production, however, was concentrated mainly in California, Indiana, Michigan, Pennsylvania, and Washington. Collectively, these States had one-half of the total operations and about three-fourths of the total output.

Most of the active operations are in 15 States in the northeastern and north-central parts of the United States, in California and Washington on the west coast, and in Florida. Small quantities of peat are produced also in Georgia, South Carolina, Colorado, Idaho, and Montana.

Individual operations vary greatly in size, but all but a few are relatively small. Of the number active in 1963, about three-fourths produced less than 5,000 tons, and most of the remainder had outputs ranging between 5,000 and 15,000 tons per year. Only a few operations are large and well-mechanized and had individual annual outputs that approached 100,000 tons. The geographic distribution and relative size of active peat operations in 1963 are shown in tables 1 and 2.

TABLE 1.—*Geographic distribution of peat operations in the United States in 1963*

Region	Number of operations	Production (short tons)
New England	5	4,941
Middle Atlantic	61	410,292
South	10	32,160
Midwest	21	48,616
West	16	82,521
Total	113	578,530

TABLE 2.—*Relative size of peat operations in the United States in 1963*

Size	Active plants		Production	
	Number	Percent of total	Short tons	Percent of total
Under 500 tons	25	22.1	5,062	0.9
500–999 tons	18	15.9	12,678	2.2
1,000–4,999 tons	44	39.0	108,552	18.7
5,000–14,999 tons	16	14.2	123,816	21.4
15,000–24,999 tons	5	4.4	88,484	15.3
25,000 tons and over	5	4.4	239,938	41.5
Total	113	100.0	578,530	100.0

Although five plants contributed 42 percent of the peat production in 1963, only one company had two active operations, and the industry was operated strictly as private enterprise. The industry receives no price supports or subsidies, and competition for markets is very keen.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Peats differ greatly in chemical and physical properties, and an adequate classification system that will identify peats according to their specific properties has not yet been devised. Peat has been classified in a variety of ways, however, and a number of descriptive terms are used to identify peats of different origin and quality. Some terms, such as "turfy," "fibrous," and "pitchy," describe texture; others, degree of decomposition; and still others, botanical origin. All, however, are very general and rather inadequate for classification purposes.

In Europe, the terms "white" and "brown" peat are used to denote a relatively undecomposed variety whose botanical origin is mainly sphagnum mosses. This type, used conventionally as a soil conditioner, is almost universally prepared by hand cutting and air drying. The more decomposed types, used generally for fuel, are referred to as "black" peat.

European peats are named also according to the manner in which they were harvested, such as cut peat, machine peat, milled peat, and hydropeat. These terms are applied particularly to the decomposed peats that are produced mainly for fuel. Other European terms are "high moor" and "low moor" peat, used generally for denoting the degree of decomposition.

For statistical purposes, the Bureau has classified peat into three general types—Moss peat, reed-sedge peat, and peat humus. Peats of the sphagnum, hypnum, and other mosses group are classified as moss peat, while those of the reed-sedge, shrub, and tree group are classified reed-sedge peat. Any peat so decomposed that its botanical identity is lost is classified as peat humus.

Although there are no established standards for differentiating peats, the sale of peat in the United States is governed by Federal trade regulations that define the requirements for labeling a product "peat" and state the manner in which the terms "peat moss" and "moss peat" may be used. Established by the Federal Trade Commission in 1950, the regulations define peat as any partially decomposed plant matter that has accumulated under water or in a water-saturated environment. It is unlawful to label a product "peat" unless 75 percent of the ma-

terial, by dry weight, is composed of peat as defined, and the remainder is composed of normally associated soil materials. A product labeled "moss peat" must conform to this definition and the peat must have been formed from sphagnum, hypnum, or other mosses. The term "peat moss," a misnomer generally applied to all types of peat, is subject to the requirements of "moss peat" except when the kind or kinds of peat of which the product is composed are conspicuously stated in conjunction with the term "peat moss."

Government purchases of peat are subject to Federal specifications, developed by the Federal Supply Service, General Services Administration. The current specification, Q–P–166e, May 10, 1961, classifies and lists the requirements for the following four types of peat: (1) Sphagnum moss peat, (2) other moss peats, (3) humus peat, and (4) reed-sedge peat.

TECHNOLOGY

Excavation and Preparation

Although virtually all peat is excavated by machinery in the United States, extraction methods and equipment differ greatly because of the various sizes of operations and the differences in physical characteristics of deposits. In general, most operators employ conventional types of excavating and earthmoving machinery, or conventional types with modifications, for extracting peat. These vary from power shovels, bulldozers, draglines, and front-end loaders, used on drained bogs, to clamshells and dredges for submerged deposits. However, a few producers have specially designed equipment similar in some respects to the types used at some of the large operations in Canada and Europe.

Peat is prepared for sale by shredding and screening and, in a few instances, by artificial drying. Processing equipment consists of a variety of screens, shredders, grinders, hammermills, and gas- and oil-fired dryers.

The following illustrate the variety of production methods employed at peat operations in the United States: In eastern Michigan, reed-sedge peat is extracted simply by loosening the top surface with disk harrows, windrowing with a V-shaped wedge, and when dry, pushing the air-dried peat with bulldozers to the edge of roads built laterally across the bog at intervals of 500 feet. Peat then is loaded into trucks by front-end loaders and transported to a storage pile at the processing plant. Before harvesting, the water level of the bog is lowered by perimeter and lateral ditching, and clay roads are built to provide a firm operating surface for trucks and loaders. The other equipment has special wide-track treads that enable it to operate upon the bog.

Preparation at this operation includes grinding and screening with hammermills, shaker screens, and belt conveyors for carrying peat and refuse. The operation also has four packaging lines consisting of automatic weighing hoppers, bag-sewing and sealing machines, and conveyors for moving and loading packaged peat, interconnected with the processing equipment. This equipment can handle various sizes of bags and each line can package and load from 12 to 28 bags per minute for shipment. One line is used exclusively for mixing and packaging potting soils, a mixture of peat, sand, and vermiculite.

In Indiana, a large deposit of moss peat is harvested by means of tractor-drawn earthmovers that scrape peat from the surface of the bog after it has been loosened by a tractor-drawn spiked harrow. The earthmovers and tractors are conventional roadbuilding and land-grading machines, modified for use on peat bogs by the installation of specially designed rubber wheels and caterpillar tracks. Prior to harvesting, the water level of the bog is lowered by ditching and trenching, but this equipment can operate only when the weather is relatively dry. This operation employs two earthmovers, each with a capacity of 4 cubic yards of peat. When full, they unload at the top of a storage pile, after which the peat is hauled by trucks to a preparation plant for shredding and artificial drying. Shredding is done by a Lindig soil shredder (standard farm machinery), and drying, by an oil-fired, horizontal, rotary kiln. This plant also has automatic packaging equipment, similar to the types employed by the operations in Michigan.

In Minnesota, a deposit of moss peat is harvested with vacuum harvesters. These are mobile machines that lift previously loosened peat by vacuum from the surface of the bog to a large tank mounted on the machine. When full, the tank is hydraulically elevated, and the peat dumped into wagons that haul it to the preparation plant. Here the peat is double-screened to remove roots, then moved by conveyor into an oil-fired, horizontal, rotary kiln. When dry, it is pulled from the dryer by suction into a storage hopper, then flows to a grinder, is again screened, and carried by conveyor to hoppers above specially designed packaging machines.

Production and preparation methods in Europe are more complex and on a much larger scale. In the U.S.S.R., where annual output is estimated at 160 million tons, peat is produced by a number of mechanized processes, of which

the principal ones are known as the machine-peat, milled-peat, and hydropeat methods. All employ a variety of large, specially designed, equipment such as ditchers, bagger elevators, milling machines, windrowing machines, and vacuum loaders, depending upon the process used. These methods of production are used also in a number of other European countries, including Ireland, Sweden, Denmark, and Finland. Processing generally includes only air drying, but, in some instances, peat is briquetted for domestic fuel, mechanically dewatered, or ammoniated for fertilizer use.

Combustion, Carbonization, and Chemical Processing

Although peat has a high moisture content when extracted, it can be air dried and burned at about the same efficiency as lignite. Peat with a moisture content of 25 percent has about one-half the heating value but twice the volume of the same weight of coal. It also has about twice the volatile content but only about one-half the fixed carbon of coal. Therefore, a conventional furnace burning peat would be required to handle about four times the volume of coal necessary for the same quantity of heat produced. Furnaces suitable for burning peat, however, can be designed with a larger grate area, greater forced draft, or a precombustion chamber.

As with other solids hydrocarbons, peat heated in ovens or retorts in the absence of air yields a solid residue, tars and tar oils, and gas. Attempts to carbonize peat economically have been relatively unsuccessful, however, and generally have been limited to laboratory and pilot-plant study.

Except for a few commercial processes for reacting peat with ammonia, such as the Humon process of Austria, the chemical processing of peat has been confined, also, to laboratory investigations.

USES

Virtually all peat consumed in the United States is used for agricultural and horticultural purposes. This applies also to imported peat, although a small quantity of the imported peat (currently 2 percent) is used for poultry and stable litter. Ninety-six percent of the domestic peat sold in 1963 was sold for general soil improvement. This peat was used chiefly by landscape gardeners and contractors for landscaping and as a base for building lawns; by homeowners for mulching and improving lawns and garden soils; and by nurseries and greenhouses. The remainder was sold for use in potting soils and mixed fertilizers; for packing flowers; for preparing seed inoculant; for golf course greens; and as a medium for growing mushrooms and earthworms.

Peat is used in Europe both for fuel and for soil improvement. For centuries peat has been cut from bogs in the shape of small blocks, air dried, and burned as domestic fuel. It still is used in this form in some countries, and large quantities also are briquetted for use as domestic and industrial fuel. But peat's greatest potential as fuel is its use for electric-power generation. Large quantities are burned in powerplants in the U.S.S.R. where it has been reported that in 1956, 30 peat-fired stations produced 11 billion kilowatt-hours of electricity, about 6 percent of the total electric energy generated. Ireland also uses large quantities of peat for fuel, consuming about 3 million tons in five peat-fired power stations in 1963.

RESERVES

The peat resources of the United States have been surveyed extensively, and known reserves are estimated at approximately 14 billion short tons of air-dried peat. The reserves are widely distributed with deposits occurring in 35 States. Approximately nine-tenths of the total, however, occurs in Florida, Michigan, Minnesota, and Wisconsin.

Table 3 shows the geographic distribution of reserves. The major deposits occur in two general areas—the northern, with about 80 percent of the total, and the Atlantic coastal, with 19 percent. The northern region covers, roughly, the area north and east of the 41st parallel and 97th meridian and includes all of the New England States, Illinois, Indiana, Iowa, Michigan, Minnesota, New Jersey, New York, Ohio, Pennsylvania, and Wisconsin. The Atlantic coastal region includes all of Florida and the coastal areas of all States south of New Jersey.

More than one-half of the U.S. reserve is in Minnesota where known deposits cover more than 5 million acres, and the recoverable reserve (deposits at least 5 feet in depth) has been estimated to be nearly 7 billion tons. Although deposits occur in virtually all parts of the State, more than three-fourths of the reserve is in four northern counties—Beltrami, Koochiching, Itaska, and St. Louis.

Wisconsin, with reserves estimated to total 2.5 billion tons, has the second largest peat resource. There are peat deposits in virtually all sections of Wisconsin, and it is estimated that peat lands cover approximately 1 million acres, with deposits ranging up to 20 feet in depth and 32,000 acres in area.

TABLE 3.—*Known original reserves of peat in the United States, estimated on an air-dried basis, by regions and States* [1]

[Million short tons]

Region and State	Reserves	Region and State	Reserves
Northern region:		Atlantic coastal region:	
Minnesota	6,835	Virginia and North Carolina	700
Wisconsin	2,500	Florida	2,000
Michigan	1,000	Other States [2]	2
Iowa	22	Total	2,702
Illinois	10		
Indiana	13		
Ohio	50	Other regions:	
Pennsylvania	1	Gulf coast [3]	2
New York	480	California	72
New Jersey	15	Oregon and Washington	1
Maine	100	Total	75
New Hampshire	1		
Vermont	8	Total all regions	13,827
Massachusetts	12		
Connecticut	2		
Rhode Island	1		
Total	11,050		

[1] Averitt, Paul, L. R. Berryhill, and D. A. Taylor, Coal Resources of the United States (Progress Report) U.S. Geol. Survey Circ. 293, 1953, p. 38.
[2] Includes Delaware, Maryland, South Carolina, and Georgia.
[3] Excludes Florida.

Michigan, the third-ranking Northern State, has a resource estimated at 1 billion tons. Michigan's deposits are well distributed throughout the State, but the largest and most extensive are in the north where some bogs cover more than 25 square miles and range in depth from 2 to 20 feet.

Several other Northern States have important deposits of peat, although the known reserve in each is less than one-half billion tons. In New York, peat lands cover approximately 800,000 acres and reserves are estimated to total 480 million tons.

All of the New England States have peat, but the largest and most extensive deposits are in Maine. Maine's reserves are estimated to total 100 million tons, of which about one-half occurs in the coastal areas and near the lower courses of major streams.

The reserve in Florida is estimated to be 2 billion tons, and there are important deposits in virtually all parts of the State. The most extensive are in the Everglades, a vast marsh area, where it is estimated that about one-half of the reserve occurs.

Some peat occurs in the Dismal Swamp area of Virginia and North Carolina, and in California, but the combined estimated reserve of both areas is less than 1 billion tons, about one-half the quantity that occurs in Florida. There are also small deposits in the coastal areas of Alabama, Georgia, Louisiana, and Texas; in Washington and Oregon on the west coast; and in Colorado, Idaho, and Montana. Less than 1 percent of the total U.S. reserve is in these States.

SOURCES OF STATISTICAL INFORMATION

Statistical data on peat are based upon annual Bureau of Mines surveys of producers. Information regularly collected includes production, sales, and use data; size of deposits; harvesting equipment used; and kind of preparation (shredding, kiln drying) prior to sale. Foreign trade statistics are collected monthly by the Bureau of the Census, U.S. Department of Commerce.

In 1958, the Bureau of the Census included peat in its periodic mineral industry survey and collected and published operational data such as employment, wages and salaries, cost of supplies, capital expenditures, and the cost of purchased machinery installed during the year. The Bureau of the Census conducted a similar survey covering the calendar year 1963, and data are being compiled presently for publication.

PRODUCTION, CONSUMPTION, AND TRADE

Peat production in the United States has increased greatly in recent years, with output in 1963 nearly three times greater than that of a decade ago. Production in 1963 was 578,530

tons, of which more than one-half was produced in Michigan, Illinois, Indiana, and Iowa. Most of the remainder was produced in California and Washington on the west coast, and in Florida, New Jersey, New York, and Pennsylvania in the East. Michigan, the chief producing State, contributed 44 percent to the total output.

Twenty percent of the production was moss peat; 53 percent was reed-sedge peat; and 27 percent was humus. Twelve percent was air dried and sold as extracted. The remainder was prepared for sale by shredding, screening, and, in a few instances, artificial drying. Approximately 54 percent of the total output was "cultivated." This is a method of reducing the moisture content by loosening the surface layer of a bog with a disk or spike harrow before the peat is removed.

Most of the peat produced in 1963 was sold, and consumption of domestic peat was approximately one-half million tons. An additional 261,000 tons of peat was imported, making apparent consumption in the United States in 1963 approximately 750,000 tons.

World production of peat was estimated to total 170 million tons. U.S. production was less than 1 percent of the world total.

Tables 4, 5, and 6 show production and consumption data for 1963 on domestic operations.

The quantities of peat imported by the United States have remained relatively constant in recent years, but imports have accounted for an increasingly smaller part of the total supply as domestic production has increased steadily. Imports currently represent about one-third of the total peat consumed annually.

About four-fifths of the peat imported in 1963 was produced in Canada. Most of the remainder was shipped from West Germany, although nine other European countries, Guatemala, Mexico, and Japan also exported small quantities of peat to the United States.

To conform with U.S. tariff regulations, imported peat is classified according to use into two grades: Poultry and stable, and fertilizer. Generally, the poultry and stable grade is imported for use as poultry and animal litter, whereas fertilizer grade is imported for various

TABLE 4.—*Peat produced in the United States in 1963, by kinds*

[Short tons]

Kind	Total	Unprepared	Processed	
			Shredded	Shredded and kiln dried
Moss	115,570	12,246	93,624	9,700
Reed-sedge	308,906	20,124	287,807	975
Humus	154,054	38,977	111,999	3,078
Total	578,530	71,347	493,430	13,753

TABLE 5.—*Production and commercial sales of peat in the United States in 1963, by States*

State	Active plants	Production (short tons)	Commercial sales		
			Short tons	Value	
				Total	Average per ton
California	5	43,873	39,873	$450,193	$11.29
Colorado	5	13,774	13,774	97,724	7.09
Connecticut, Maine, Massachusetts	5	4,941	4,441	58,933	13.27
Florida	7	22,143	21,049	129,380	6.15
Georgia, Maryland, South Carolina	5	11,642	10,998	112,640	10.24
Idaho, Montana, North Dakota	3	2,070	1,320	24,550	18.60
Illinois and Iowa	4	21,732	21,732	239,939	11.04
Indiana	6	55,745	47,695	411,848	8.64
Michigan	28	255,859	251,809	2,412,995	9.58
Minnesota	6	8,373	8,110	294,373	36.30
New Jersey	3	23,685	23,685	241,042	10.18
New York	5	21,358	21,358	177,664	8.32
Ohio	10	7,110	6,910	108,876	15.76
Pennsylvania	7	44,910	33,952	338,667	9.97
Washington	11	38,648	37,248	187,549	5.04
Wisconsin	3	2,667	2,667	136,504	51.18
Total	113	578,530	546,621	5,422,877	9.92

TABLE 6.—*Commercial sales of peat in the United States in 1963, by uses*

Use	In bulk			In packages			Total		
	Short tons	Value		Short tons	Value		Short tons	Value	
		Total	Average per ton		Total	Average per ton		Total	Average per ton
Soil improvement	255,318	$1,728,661	$6.77	268,589	$3,130,099	$11.65	523,907	$4,858,760	$9.27
Potting soils [1]	5,169	31,588	6.11	6,718	410,831	61.15	11,887	442,419	37.22
Packing flowers, shrubs, etc.	4,176	36,427	8.72	2,161	30,663	14.19	6,337	67,090	10.59
Mushroom beds [2]	1,426	14,034	9.84				1,426	14,034	9.84
In mixed fertilizers	3,064	40,574	13.24				3,064	40,574	13.24
Total	269,153	1,851,284	6.88	277,468	3,571,593	12.87	546,621	5,422,877	9.92

[1] Includes small amount sold for seed inoculant.
[2] Includes small amount sold for earthworm culture.

TABLE 7.—*Peat moss imported for consumption in the United States in 1963, by kinds and by countries*

Country	Poultry and stable grade		Fertilizer grade		Total	
	Short tons	Value	Short tons	Value	Short tons	Value
North America:						
Canada	4,135	$248,500	206,649	$10,038,335	210,784	$10,286,835
Guatemala	7	358			7	358
Mexico	40	4,239			40	4,239
Total	4,182	253,097	206,649	10,038,335	210,831	10,291,432
Europe:						
Denmark	17	767	212	9,736	229	10,503
Finland			123	5,240	123	5,240
France			7	368	7	368
Germany, West	[1] 1,273	55,440	34,099	1,411,885	35,372	1,467,325
Ireland	62	2,200	2,293	88,993	2,355	91,193
Netherlands	84	3,959	1,558	57,993	1,642	61,952
Poland and Danzig			6,786	247,017	6,786	247,017
Sweden			3,677	171,173	3,677	171,173
Portugal			124	2,000	124	2,000
United Kingdom			130	5,345	130	5,345
Total	1,436	62,366	49,009	1,999,750	50,445	2,062,116
Asia: Japan	4	2,085	51	1,924	55	4,009
Grand total	[1] 5,622	317,548	255,709	12,040,009	261,331	12,357,557

[1] Adjusted by Bureau of Mines.

Source: Bureau of the Census.

types of soil improvement. Of the total imports in 1963, 98 percent was classified fertilizer grade and entered the United States duty free. A duty of $0.25 per long ton was levied on peat classified poultry and stable grade.

Table 7 shows imports of peat moss, by kinds and by countries, in 1963. No peat is exported from the United States.

MARKETING AND PRICES

Before 1955 most domestic peat was sold locally in bulk because packaging materials in which peat could be packaged and shipped economically had not been developed. (Unlike the moss peats of Canada and Europe, most of the peat produced in the United States has a texture that makes it unsuitable for baling.) With the advent of synthetic films, inexpensive moistureproof containers became available, and large quantities of domestically produced peat are now packaged and distributed in virtually all parts of the United States.

More than one-quarter million tons, or 51 percent of the total peat distributed in 1963, was sold in packages. Packaged peat usually is distributed through normal wholesale and retail channels and is available in retail outlets such as garden centers, hardware, drug and variety stores, and food supermarkets in virtually all parts of the country. Bulk peat usually is sold directly to consumers by the producer.

There is no standard unit of measurement for selling peat in the United States, but most peat sold in bulk is air dried and sold by the cubic yard. Packaged peat, which can be either air- or kiln-dried, is sold by both volume and weight. Most packaged peat is sold on a weight basis, however, principally in units of 25, 50, and 100 pounds. Preferred containers are polyethylene-lined paper bags. Some peat is packaged also in heavy-gage synthetic bags and burlap bags with synthetic-film liners.

Prices of domestic peat vary greatly, but, in general, the sales value depends chiefly upon the kind of peat, the degree of processing, and whether the peat is sold in bulk or packaged. In most instances, the value of packaged peat is about double that of bulk peat. Packaged peat usually has undergone more processing, and more labor and equipment are required to produce the packaged product.

The values of domestic and imported peats are shown in table 8. For domestic peat, the values are equivalent to the total amount producers realized from sales, f.o.b. plant, except that for packaged peat the cost of bags or containers was not included. The average price per ton for all domestic peat sold in 1963 was $9.92. The average plant price of bulk peat was $6.88 per ton while the unit price of packaged peat was $12.87.

The average value of $47.29 per ton of imported peat was about five times greater than that of domestically produced peat, but the values are not comparable because they were assigned at different marketing levels. Values assigned to imported peat were established at the port of embarkation and were approximately equal to prices paid by importers, less

TABLE 8.—*Quantity and value of domestic peat sold in the United States, and the quantity and value of peat imported*

Year	Domestic peat			Imports		
	Short tons	Value	Average value per ton	Short tons	Value	Average value per ton
1957–59 (average)	342,711	$3,556,551	$10.38	267,525	$12,300,753	$45.98
1960	430,664	4,456,510	10.35	263,887	13,509,015	51.19
1961	492,798	4,672,933	9.48	252,437	13,178,474	52.21
1962	566,441	5,185,627	9.15	267,678	12,868,168	48.07
1963	546,621	5,422,877	9.92	261,331	12,357,557	47.29

transportation and other miscellaneous charges. In some instances, ocean freight and other nondutiable charges such as insurance may have been included inadvertently.

In contrast to most packaged domestic peats which are more decomposed, have a relatively high moisture content, and are sold by weight, imported peats are light and fibrous, usually are pressed into bales or compacted into synthetic-film containers, and are sold on a volume basis. To indicate respective densities, each 100 pounds of a typical air-dried imported peat will measure approximately 12 bushels, whereas 100 pounds of a typical air-dried domestic peat will measure only 3 or 4 bushels. However, a few U.S. operations produce peat with properties similar to the imported types. In 1963, a 100-pound bag of domestic reed-sedge peat could be purchased at retail in the Washington, D.C., area for $1.69; a 7½-cubic-foot bale of imported peat, weighing from 80 to 100 pounds, had a retail price of $4 to $5 in the same area.

EMPLOYMENT AND PRODUCTIVITY

Employment in the peat industry is seasonal, as production and processing at most operations cease during the winter months. Of the 113 active plants that reported production to the Bureau for 1963, 656 employees worked a total of 942,430 man-hours, or an average of 1,437 hours per employee during the year. On the basis of an 8-hour day, the total number of man-days worked during the year was 117,804. Related to production, this was an output of 4.91 tons per man-day for 1963.

RESEARCH

Most of the research on peat is conducted in a number of northern European countries where peat is used in large quantities for fuel. Most of these countries consider peat a major organic raw material and, in addition to developing peat as a fuel for heating and electric-power generation, they have attempted to find practical methods for converting peat to metallurgical fuel, for using peat for the production of town gas, as a source of chemical materials, and as a base for enriched fertilizers.

The Soviet Union undoubtedly conducts the greatest amount of research on peat. In addition to having a large number of laboratories and experiment stations that are concerned solely with the development and use of peat, the U.S.S.R. has established several peat institutes, which not only train engineers and technicians, but conduct large-scale investigative programs ranging from basic research to applied research and development.

The Moscow Peat Institute, which was established in 1930 under the Ministry of Higher Education, is the principal Soviet institution for the training of technical personnel for the peat industry. This establishment not only graduates from 250 to 300 peat engineers per year, but also conducts a broad research program encompassing such areas in 1962 as the hydraulics and hydrotechniques of peat installations, classification and characteristics of peats, radioisotope techniques in the study of the physical and mechanical properties of peat, technology and equipment of hydropeat installations, and the chemical technology of peat.

The All Union Institute in Leningrad is the central research organization of the Soviet peat industry. This institute, which was founded in 1935 and is an agency of the Ministry of Power Stations, has three prime objectives: (1) The full mechanization of the peat-for-fuel industry as well as the mechanization of plants for the production of chemicals and other by-products from peat, (2) the development of new methods of producing and dewatering peat, and (3) the modification and improvement of existing techniques of winning peat. The institute has several departments that include a number of laboratories, a design department, shops, and library.

Peat in Ireland is produced under the auspices of Bord na Mona, a statutory corporation set up by the Irish Parliament in 1946 to develop peat resources, with particular emphasis on peat for electric-power generation. An important part of the Bord na Mona organization, an experimental station at Droichead Nua, County

Kildare, was established to develop improved methods for winning and utilizing peat. Although the work of the experimental station was designed originally to develop more efficient harvesting methods and improved burning equipment for power generation, research programs have been expanded, and this organization now engages in research aimed at developing peat as a raw material for the production of chemicals, coke, and waxes.

Austria, Finland, France, Germany, Holland, and Sweden also have active peat research programs. Most are concerned with developing improved techniques for using peat as a fuel, but, as in Ireland, these countries are attempting also to use their peat resources as a base for developing new products and establishing new industries.

There has been little emphasis on peat research in the United States because of the abundant supply of other fuels and other raw material sources of chemicals. Minnesota, however, has sponsored several research projects on peat in an attempt to find ways of economically using Minnesota's vast peat resources. Through the Iron Range Resources and Rehabilitation Commission, a State agency, a "Chemical Products from Peat Project" was established at the University of Minnesota in 1954. This project, which has been engaged in developing basic knowledge of the peats of Minnesota from the standpoint of eventual economic use, has conducted investigations ranging from basic through applied research, including studies such as the use of peat as a binder for pelletizing taconite, and the application of peat to agriculture and horticulture.

The Bureau of Mines made several studies many years ago on the potential of peat as a source of energy, but concluded that peat could not compete economically in the United States with other fuels.

OUTLOOK

The outlook for the U.S. peat industry is expected to be one of continued growth. Since 1945 the number of producers has more than doubled and domestic output has increased more than five times. Including imports, annual consumption is rapidly approaching 1 million tons. Consumption in the United States should continue upward because peat is in demand by homeowners, landscape gardeners, nurseries, and greenhouses in most parts of the country, particularly in urban and suburban areas. In past years, animal manures were used extensively as a source of organic matter for soil improvement. These, however, have become virtually unavailable in many areas, and peat generally has become accepted as an economic and lasting substitute when used in conjunction with other fertilizer materials.

Consumption of domestic peat for special agricultural and horticultural uses other than general soil improvement (potting soils, packing flowers, mushroom beds, and so forth) has increased moderately in the past decade and should continue upward, probably at a rate consistent with population increases. The use of peat as a filler for mixed fertilizers, however, has been decreasing steadily and probably will continue to decline.

Despite the large-scale use of peat for fuel in a number of European countries, peat cannot compete as a fuel in the United States with other fuels that are available at lower cost in virtually all areas. Peat, therefore, will not be used for fuel in this country in the forseeable future, except possibly in minor quantities in local areas if more efficient production and processing methods are developed.

PROBLEMS

Expansion of the peat industry in some States is limited by the remoteness of their operations from established markets. Generally speaking, it is uneconomical to transport most of the types of peat used for soil improvement long distances because peat is a bulk item with a relatively low value. Therefore, to be competitive, a peat operation must be located in an area where markets exist, or in an area from which peat can be shipped to markets at low rates of transportation. Several States presently producing peat have a market disadvantage because of their geographical location. This disadvantage possibly may be overcome by developing more economical and more efficient harvesting and drying methods.

A continuing problem of both producers and consumers is the lack of an adequate classification system for identifying the various types of peat. The present and most generally accepted system, which groups peats according to botanical origin, is overlapping and does not recognize their different chemical and physical properties.

This problem currently is being resolved by American Society for Testing and Materials Committee D–29, which was organized in 1963 to stimulate research and formulate definitions, methods of test, and specifications relating to peats, mosses, humus, and related products.

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PERLITE

By Timothy C. May [1]

PERLITE is a siliceous rock containing 3 to 5 percent water. When it is crushed and heated, the rock expands to a mass of glass bubbles, producing a lightweight aggregate with many sealed cavities, which retard the conduction of heat and sound when used as loose fill or as aggregate in concrete and building plaster. Other uses include filter aid, horticultural applications, oil well cementing and grouting, filler, catalyst support, and abrasives.

Substantial commercial production started in 1946, and in 1963 404,000 tons of crude perlite was mined. The output of expanded perlite in 1963 was 272,000 tons, valued at $14.5 million. Production of crude perlite came from seven Western States, the major portion from New Mexico.

The principal industry problems are keeping pace and gaining a share of the fast growing market, high transportation costs of crude perlite to eastern markets, health hazards, and minimizing production of fines.

The domestic reserve of perlite is adequate to meet foreseeable requirements.

BACKGROUND

Perlitic obsidian reportedly was expanded and used for the manufacture of abrasive bricks in Germany before 1925. In 1940 perlite was expanded experimentally in a kiln at Las Vegas, Nev., and used with gypsum for building plaster. About 1941, crude perlite from Picket-Post Mountain near Superior, Ariz., was flash-popped in an experimental gas-fired furnace. This led to a series of small plants experimenting with the treatment and use of expanded perlite (*5*) [2]

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

In 1946 the first commercial output was reported by five companies, totaling 4,200 tons from four mines in the Superior, Ariz., district and one near Beatty, Nev. In 1947 a property on the Deschutes River in Wasco County, Oreg., started producing. The post World War II building boom stimulated demand, and other perlite mines were opened. In less than a decade perlite changed from a lithologic curiosity to an important building material.

Perlite from a deposit in northern Ireland is largely shipped to England for expanding. A mine in Sardinia sends its ore to Milan, Italy, for processing. Otherwise very little foreign perlite mining is reported.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

In commercial usage the term "perlite" refers to any naturally occurring glass of igneous origin that will expand, when quickly heated, to yield a frothy, light-colored mass of glass bubbles. The term is also applied to the expanded product.

The petrological definition of perlite is restricted to volcanic glass which has a concentric, or "onion," structure of fracturing (*5*). This structure of fracturing is also known as perlitic.

Other characteristics of commercial crude perlite are 3 to 5 percent water of composition, waxy to pearly luster, transparent to translucent at thin edges, rhyolitic in composition. It is essentially an amorphous aluminum silicate of volcanic origin. An average analysis, in percent, of 10 perlites from 6 currently producing States follows (*1*):

[1] Commodity specialist.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

	Percent
Moisture loss at 105° C	0.2
Total moisture loss after ignition at 800° C	3.83
Aluminum oxide (Al_2O_3) (including any phosphorus pentoxide or manganese oxide)	13.08
Calcium oxide (CaO)	.72
Iron oxide (Fe_2O_3)	.89
Magnesium oxide (MgO)	.18
Potassium monoxide (K_2O)	4.44
Silicon dioxide (SiO_2)	73.2
Sodium monoxide (Na_2O)	3.31
Sulfur trioxide (SO_3)	.04
Titanium dioxide (TiO_2)	.09

Before expanding, crushed and sized crude perlite ore has a bulk density ranging from 65 to 75 pounds per cubic foot. The approximate densities of expanded perlite may range from 3 to 4 pounds per cubic foot, for use as lightweight cast insulating slabs, to 8 to 20 pounds per cubic foot or more, sized for concrete aggregate.

Expanded perlite ranges from a fluffy, highly porous material to glazed particles having almost no porosity.

For interior plaster aggregate, where light weight, good insulation, and acoustical qualities are more important than low porosity, a satisfactory particle-size range for raw ore is 100 percent through 8-mesh, with not more than 5 to 10 percent through 100-mesh and substantial proportions in the range from 30- to 60-mesh. For exterior stucco and precast masonry concrete, a suggested grading is 100 percent through 4-mesh, with 10 to 15 percent maximum through 100-mesh and the intermediate range as nearly one size as possible. This latter grading can produce a concrete with 1,000 to 2,000 pounds per square inch compression strength after 28 days with 6 to 12 pounds of water absorbed per cubic foot of concrete and a weight of 40 to 70 pounds per cubic foot for the concrete when air dried.

The suitability of expanded perlite aggregates is usually determined by trial. Standard test specimens of perlite concrete and plaster are prepared and tested for compressive strength and other physical properties.

The Perlite Institute, Inc., New York, N.Y., has published tables showing typical mix designs for perlite insulating concretes and plaster with the corresponding physical properties of these products (*7*).

TECHNOLOGY

Geology

Petrographically, perlite and other volcanic glass may be essentially free of crystalline material, although most natural glass contains microscopic crystallites and large phenocrysts; the latter range from 1 percent by volume to 50 percent or more in rocks known as vitrophyres. If crystallization progresses, the glass may become crowded with minute grains throughout the mass, or with stratifications almost microscopic in thickness. Silicification or opalization of the glass can also occur. The presence of crystals and devitrification products in any appreciable quantities in volcanic glass often produces a noncommercial perlite.

Factors that affect the physical and chemical characteristics of volcanic glasses include water content, rate of cooling, and age. Volcanic glass often becomes devitrified by the effects of steam from fumaroles or hot springs. It also devitrifies in time under normal conditions, as witnessed by the changes of manufactured glass objects found in prehistoric Egyptian tombs. Hence very few occurrences of undevitrified glass older than Cretaceous are known.

The color of volcanic glass ranges from black, through shades of red, green, and brown, to nearly white. While some glasses break with a conchoidal fracture, others have the well-known, closely spaced concentric fracture patterns, or "onion" structure. Some glasses have a columnar or prismatic jointing that may yield a needle structure, while others contain vesicles and show strong flow structure, approaching pumice.

Some deposits of perlite and pitchstone are intrusive, occurring as dikes, sills, and quickly cooled zones in the margin of other intrusive bodies. The most important current production, near Tres Piedras, N. Mex., comes from an extensive flow, almost 1,000 feet thick, which has been eroded into several individual island remnants. The hardness is between 5.5 and 7; specific gravity ranges from 2.2 to 2.4, and weight ranges from 139 to 150 pounds per cubic foot. Volcanic glasses are a product of igneous processes within the earth's crust, and the combined water is evidently from the original magma.

As domestically occurring undevitrified siliceous volcanic rocks are found only in the West, all known deposits of perlite occur there. Although rare occurrences of volcanic glass are known in volcanic strata as old as Cretaceous, most glasses are found in beds of Tertiary or Quaternary age. Rocks of similar composition that were formerly true glasses, but from older series, are now thoroughly devitrified and thus have lost their expansion qualities. (*3–5*, *9*).

Mining

The perlite deposits are massive lava flows, sometimes several hundred feet thick and extending over hundreds of acres. Because of the

areal extent, pits are usually kept shallow to maintain low mining costs.

All perlite mining is done from open pits, and the first step is the removal of overburden when present. Although blasting is occasionally employed, mining more frequently consists of loosening the rock with bulldozers equipped with rippers and excavating with carryalls, power shovels, or bulldozers moving ore to loading chutes. To insure uniformity in the quality of perlite ore, the open face operation mines in a lateral section, in contrast to conventional open pit mining. Because of the low unit value of crude perlite, only those deposits that can be mined cheaply are operated.

Processing

Ore from the mines is trucked to the mill where it is dumped on a grizzly and usually falls to a jaw crusher. The ore in a typical plant is then raised by bucket elevator to a storage bin, from which it goes by apron feeders to a direct-fired cylindrical rotary dryer. Drying improves efficiency of screening and air classification.

From the dryer a bucket elevator raises the ore to enclosed vibrating screens, the oversize going to a secondary crusher. Undersize drops to mechanical-air classifiers for removal of the excessively fine fractions, which are detrimental to the final product. After dust removal, the products go to bins where different-size shipping products are stored.

Perlite ore is usually processed dry because water is scarce in many perlite mining areas; also drying a wet-processed product costs more.

Perlites, which crush to particles approaching a cubic shape, expand to a more uniform size range. However, shape cannot be closely controlled, because perlite tends to break along preexisting fractures.

The expansion of crude perlite is influenced by (1) the amount of originally combined water present, (2) the amount of this combined water retained when the softening point is reached, (3) the rate of heat application, (4) the maximum temperature reached, (5) the structure of the perlite including fractures, (6) the size distribution of the crude ore particles furnaced and (7) the softening point of the crude perlite.

In expansion the temperature at which the glass is just soft enough to be plastically deformed by the expanding steam ranges from 1,400° F for some perlite to 2,000° F for others. A high frequency of parting planes increases the formation of fines. Some perlites explode on heating because of weaknesses in the rock.

The unexpanded particles are dropped through the fast-moving flame of the gas- or fuel oil-fired furnace. Optimum conditions are difficult to attain, especially when the feed is coarse. As the softening point is reached, the release of part of the combined water raises the eutectic temperature and causes resolidification unless the heat is correspondingly increased. If not adequately increased, larger particles may be ejected from the furnace before the heat has penetrated to their centers (*10*).

Two types of furnaces are now used for expanding perlites.

The horizontal rotary furnace usually has three metal shells. A hot flame inside the inner shell chamber gives sufficient heat to preheat the ore as it travels between either of the two outer shells. Preheat temperature ranges from 400° to 600° F. A scoop attached to the revolving furnace picks up the raw ore, and helical flights move the ore through the preheater and then into the inner chamber of the furnace, where it meets the flame and where the direction of ore travel is then reversed. The flights in the inner furnace chamber repeatedly lift the ore and drop it through the flame area, and as the ore particles are lightened by expansion the air pressure from the burner vent blows them out of the furnace.

The discharged expanded perlite is raised in the hot gases by a suction fan to a collection cyclone and one or more smaller auxiliary cyclones. This collection system separates the fine and coarse products and permits a relatively clean air discharge to the atmosphere.

The vertical furnace is essentially a vertical tube with maximum dimensions of about 1.5 feet in diameter by 18 feet high. An inner shell of high-temperature alloy steel surrounds the expansion chamber, insulated by refractory brick or an air space.

As the product of the expanding furnace enters a collection cyclone, 10 to 30 percent of the expanded fine perlite is carried over with the hot gases to one or more smaller, high-efficiency cyclones that allow clean air and hot gases to discharge. Material not carried from the collection cyclone by the gases drops to a pipe where it is met by a stream of cold air. This cools the product and also transports it through the plant.

The fine material collected in cyclones is either recombined with the cooled product and sent to the bagging plant or sent to waste if this product is too fine to be salable. Some plants are equipped with a baghouse to collect dust escaping the cyclones. The abrasion of dust

particles rapidly deteriorates screens, bearings, and other moving parts.

Gas and air should be well mixed if gas burners are used, and when using fuel oil, a finely atomized oil-air dispersion is required. Many ordinary burners are not suitable because the perlite feed tends to extinguish the flame. Use of a burner collar, just in front of the burner nozzle, to radiate heat onto the flame, helps to maintain combustion.

USES

About 60 percent of the expanded perlite produced in the United States in 1963 was used for construction purposes. The 1963 use of expanded perlite, computed from a Bureau of Mines canvass, follows:

	Percent
Building plaster aggregate	39
Filter aids	15
Concrete aggregate	12
Oil well cement	4
Insulation (loose fill)	4
Miscellaneous uses	26

Owing to its lightweight and heat-insulating advantages, perlite has become a major aggregate in gypsum plaster. When mixed with gypsum and water in lieu of sand, perlite creates a plaster that can be troweled or sprayed on lath to form a resilient wall or ceiling that can withstand stresses and thermal changes. Mill mixing of perlite plaster has become a major feature of the industry in recent years.

Because of its low specific gravity, perlite has advantages as a raw material for the manufacture of filter aids. Perlite is particularly adapted for situations where high flow rate is more important than clarity of the filtrate. Perlite filter aids are now being used to filter various food products, beverages, chemicals, resins, pharmaceuticals, and other liquids.

Perlite lends itself to the preparation of lightweight aggregate insulating concrete. The most common use is in roof deck construction where the structural deck and insulation can be combined in one lightweight slab that needs no further insulation. Perlite concrete also is being used as a floor fill in multistory buildings, in insulating concrete blocks and tilt-up panels, and as exterior insulating walls sprayed as a backup for metal panel facings.

Oil well cementing and grouting present a growing market for expanded perlite. It prevents lost circulation of drilling lubrication fluids by bridging openings in the wellhole walls.

Substantial quantities of expanded perlite are used annually in soil conditioning, as a plant growing medium, as packing material for shipment of nursery stock, and as a carrier or diluent for herbicides and insecticides.

Expanded perlite with bulk densities below 4 pounds per cubic foot is used as insulation in the form of loose fill. Poured in the hollow centers of concrete block or between wall studs, it is a very effective insulator. In this loose form, it is used for imbedding hot steel ingots during transportation, for packing containers of liquid air, and as foundry sand to prevent rapid cooling in the mold. Packed in batts or jackets, it is placed around steam and refrigeration pipes. It is also used in lining refrigerators, refrigertor cars, cold storage space, and frozen-food shipping boxes.

Perlite has been used successfully as a porous support for catalysts and reagents in various chemical reactions. It also has some application as an abrasive and as a refractory in the medium temperature range.

The uses for perlite fines include fillers or extenders in rubber, paints, enamel, glazes, plastics, paper, textiles, resins, cleansing compounds, and tile.

Within the past few years perlite powders have become widely used in cryogenics. Perlite has proved a most effective insulator at temperatures below −150° C and is now used extensively for insulating tanks containing liquid gases such as oxygen and hydrogen (*2*).

ALTERNATE MATERIALS

Perlite encounters several long-established competitive commodities in all its fields of use. As plaster aggregate it must compete with silica sand, exfoliated vermiculite, and pumice. Competitive concrete aggregates are the heavy materials, such as sand, gravel, crushed stone, and slag, and lightweight aggregates, which include expanded clay, shale and slag, exfoliated vermiculite, cinders, pumice, sawdust, organic fibers, and diatomaceous earth. Air entraining agents, which lighten concretes, can also be considered a lightweight aggregate substitute. Mineral wool, exfoliated vermiculite, pumice, and diatomite compete in the loose-fill category.

In oil well cementing, vermiculite and clays, including bentonite, are competitive materials.

There are many fillers and extenders with which perlite must share the market. Some of these are feldspar, gypsum, pumice, mica, talc, limestone, kaolin, silica sand, diatomite, exfoliated vermiculite, barite, and synthetic calcium silicates. Most of these require fine grinding when used as fillers.

In filtration diatomite is the principal competitive material, while silica sand is used in

large-scale filtering of coarse sludges, for which perlite is only seldom used.

RESERVES

Few data have been published on the reserves of perlite in the United States. However, estimated figures published by a few companies indicate reserves amounting to more than 150 million tons (*5*). Extensive resources occur in Arizona, California, Colorado, Idaho, Nevada, and New Mexico, and to a lesser extent in other Western States. Perlite occurrences in Alaska also have been described (*11*). The total reserves of usable perlite are adequate for any foreseeable requirements. Foreign perlite deposits occur in New Zealand, western Canadian Provinces, Sardinia, Northern Ireland, Mexico, Japan, Greece, Iceland, Australia, Italy, France, Turkey, and the U.S.S.R.

SOURCES OF STATISTICAL INFORMATION

The available commercial statistics on perlite are essentially limited to domestic figures. There are scant records of foreign trade or foreign production of perlite. The Bureau of Mines canvasses producers of both crude and expanded domestic perlite annually, and the Census of Mineral Industries provides industrial data on perlite for a single year intermittently.

PRODUCTION, CONSUMPTION, AND TRADE

Disregarding change in stocks, there was a difference of 33 percent between the weight of total crude perlite produced and expanded perlite output in 1963. This difference is partially due to fines formed in the somewhat explosive expanding process and also to fused and unexpanded particles removed from the furnace. Statistics on stocks are not collected by the Bureau of Mines or the Perlite Institute, but accumulations of currently unmarketable fines are large.

Nevada was the first State to record production of crude perlite, but New Mexico has been the leading producer since 1951.

In 1963 California, with 14 expanding plants, had the largest number of processing operations, followed by Pennsylvania and Texas with 6 each, Illinois and New York with 5 each, and Colorado, Florida, Indiana, Iowa, and New Jersey, each with 3 plants.

Table 1 shows statistics for crude and expanded perlite produced and sold or used during 1954–63.

TABLE 1.—*Crude and expanded perlite produced and sold or used by producers in the United States*

[Thousand short tons and thousand dollars]

Year	Crude perlite						Expanded perlite		
	Quantity mined	Sold		Used at own plant to make expanded material		Total quantity sold and used	Quantity produced	Sold	
		Quantity	Value	Quantity	Value			Quantity	Value
1954–58 (average)	348	190	$1,690	92	$634	282	239	238	$12,174
1959	443	221	1,846	104	891	325	276	273	14,187
1960	385	214	1,847	98	818	312	248	244	13,046
1961	374	196	1,665	114	998	310	240	235	12,605
1962	408	198	1,611	122	1,052	320	238	234	12,536
1963	404	203	1,631	122	1,096	325	272	270	14,497

In 1953 the Bureau commenced canvassing the industry to determine the relative consumption of expanded perlite for various uses. From 1953 to 1958 consumption in building-plaster aggregate increased from 141,000 tons to 155,000 tons; it dropped to 105,000 tons in 1963. Aggregate construction concrete increased from 18,000 tons in 1953 to 38,000 tons in 1958 and decreased to 32,000 tons in 1963. Filter aid consumption was 4,500 tons in 1953 and increased to 26,000 tons in 1958, with a further increase to 42,000 tons in 1963.

There are no published government records of specific imports of perlite. Crude perlite is exported to Canada, but no record of shipments is available.

Crude perlite may be imported duty free, and expanded perlite is dutiable at 15 percent ad valorem.

STRATEGIC CONSIDERATIONS

The United States is self-sufficient in perlite. All 1963 production of crude came from seven Western States; other Western States have un-

developed occurrences. Imports of crude to eastern seaboard areas seem likely in the future because ocean freight from some foreign sources may be less than rail freight from western domestic mines.

PRICES

The average unit value of crude perlite sold by miners to expanders in 1963 was $8.05 per ton, crude used for expanding by prime producers had an average unit value at crushing plants of $8.94 per ton. The average price of expanded perlite in 1963 was $53.69 per ton, and the 1959–63 average was $53.36.

TAXES

No special taxes are imposed on the perlite industry. Crude perlite producers are allowed a depletion allowance of 10 percent on domestic and foreign production.

TRANSPORTATION

Crude perlite is produced in seven Western States, the easternmost being Colorado. Transportation therefore plays a major role in the distribution of costs. In 1963 carlot shipments of crude perlite from Antonito, Colorado, to the eastern seaboard were: Washington, D.C., $12.99; Boston, Mass., $14.49; Trenton, N.J., $13.39; and Jacksonville, Fla., $13.57. Ore freight rates, in these costs represent over 60 percent of the total delivered cost to expanders.

RESEARCH

The Perlite Institute has sponsored research on physical, thermal conductivity, acoustical, and fire properties of perlite. Fire tests sponsored by the Institute have resulted in a wide variety of fire ratings for lightweight concrete and plaster constructions. Investigations have been sponsored at universities and independent laboratories which have developed data on perlite for use as insulation at low and high temperatures, as a plastics extender and fertilizer carrier (*7*).

Some research was done by the Bureau of Mines on the composition and physical properties of perlite and thermal data and energy required in expansion. Details were reported in three publications (*1*, *6*, *8*).

OUTLOOK

Perlite consumption will depend to a great extent on the increase of residential and industrial construction. Trends in the production of expanded perlite indicate a slight increase in the rate of growth. In 1958, 292,000 short tons of crude perlite was sold or used by producers compared with 325,000 in 1963. Expanded perlite production increased 13 percent during 1958–63. Such a rate of increase indicates the continuing growth of the perlite industry.

Trends in the use of expanded perlite as a replacement of sand in building plaster indicate a reversal in the rate of growth. Use as a filter aid is expected to increase. It is expected that perlite will continue to take over a portion of the filter aid market now held by the diatomite industry. Although the greatest usage of perlite today is in the construction industry, it has a large market as a filtration medium, additive, thermal insulator, soil conditioner, and carrier for insecticides and weed killers. Over the short terms period (5 to 10 years) consumption of expanded perlite is expected to increase 3 to 5 percent per year.

Building code authorities have recognized the official fire ratings on perlite insulating concrete. This will permit a broader use of lightweight aggregate and will encourage the use of perlite. There is a growing trend to use silicone-treated perlite for loose fill insulation.

Many deposits of perlite have been discovered, but estimates of total reserves are not available. The many millions of tons of usable perlite presently known, however, indicate that supplies are adequate for any foreseeable demand. Because perlite is found only where recent volcanic activity has occurred, discovery of perlite deposits in the Eastern United States seems unlikely. Foreign sources may in the future supply some eastern areas, because of the high cost of rail freight from the Western United States.

Growing use in cryogenics is expected. Perlite has proved an effective insulator at temperatures below −150° C.

PROBLEMS

One of the principal problems of the perlite industry is to hold and to expand its share of the filter aid market.

More information is needed on the technology of perlite processing. Many advances have been made but they have not been adequately documented in available literature.

The perlite industry needs to utilize the fines produced during the various perlite processing steps. These fines might be used in place of finely ground limestone for white pigmentation. Specially graded perlite now is purchased by many companies to produce fines for use in pigments.

High transportation costs of crude perlite to expanders in eastern and northern sections of the United States invites competition, to some extent, from alternate materials. Substantial savings have been realized, however, on 100 ton shipments.

The mining and processing of perlite creates a dust hazard. The advent of air pollution controls in many cities has resulted in the installation of dust collection systems in most perlite plants.

The majority of companies engaged in the production of expanded perlite are relatively small and marketing and distribution over a large geographic area presents a problem.

The low value of crude perlite restricts mining to deposits amenable to low-cost open-pit exploitation. Cost limitations also eliminate many deposits in which variations in quality necessitate highly selective mining.

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PETROLEUM AND NATURAL GAS

By R. F. Zaffarano [1] and J. D. Lankford [2]

A LITTLE over a century ago in 1859, when Edwin L. Drake discovered petroleum in the first commercial well at Titusville, Pa., he unleashed the potential of one of Nature's versatile commodities. The industry has grown to the point where petroleum and natural gas and their hydrocarbon derivatives now supply three-fourths of all the U.S. fuel energy needs. World consumption of petroleum continued to increase in 1963; in the United States the increase was about 6 percent annually, and in the rest of the free world the increase was about 10 percent. The estimated proved reserve of recoverable liquid hydrocarbons in 1963 in the United States included 30.9 billion barrels [3] of crude petroleum and 7.7 billion barrels of natural gas liquids. The worldwide reserve increased to a record high of 326 billion barrels. Five-eighths of the world reserve is in the Middle East, where the 1963 output was 6.8 million barrels daily.

The importance of Middle East oil reserves is clearly shown by the announcement that increased on-site facilities in the world's largest known oilfield, Ghawar in Saudi Arabia, will enable that field to increase its daily production to 800,000 barrels. This production approximates the combined daily crude-oil production of Oklahoma and Kansas. Such prolific production in view of the continued increased growth rate of foreign petroleum consumption (approximately 60 percent greater than the U.S. demand) has influenced many U.S. companies to divert their exploratory efforts abroad. Thirty-two leading U.S. companies derived $39.2 billion in revenue from their worldwide operations in 1963—an increase of 7 percent over that of 1962.

In the United States the demand for natural gas has shown a phenomenal growth in the past 20 years, with an average increase of 5.8 percent per year for the last decade. Natural gas and natural gas liquids provided 34.2 percent of the total energy utilized in the United States in 1963. Marketed production of natural gas reached 14.7 trillion cubic feet in 1963.

Natural gas proved reserves in the United States at the end of 1963 amounted to 276 trillion cubic feet. World reserves of natural gas are considered indeterminate at present.

Natural gas consumption outside this country has been limited because of poor access to markets. This is being remedied to some extent in the newly developed gasfields in North Africa where liquefied methane is shipped to Western European markets in special insulated and refrigerated tankers. Huge new offshore gas reserves in the Netherlands are slowly being developed for European energy markets, formerly the sole domain of solid and liquid fuels.

The international petroleum industry is experiencing a supply-demand race for world markets. Middle East fields alone in 1963 almost equaled the combined production of the United States for the first time in history. They are expected to accomplish this task in 1964. The continued advantage of foreign sources, because of the lower costs for finding and developing crude oil compared to domestic costs, has provided the necessary incentive to U.S. producers to invest and participate increasingly in foreign operations. Companies are willing to forego high initial costs to pioneer foreign area markets because of the strong and growing world demand. The advantage is about $1 per barrel in finding-producing cost below that in the United States.

The domestic petroleum industry has been working diligently to improve its economy. Research efforts are under study on technical problems covering the entire range of oil and gas activities. Improvement in the recovery from oil and gasfields is a major study area. On the average, only 30 to 35 percent of the oil discovered is recovered before the economic limit is reached. Likewise, numerous petroleum resources are submarginal economically and cannot be produced with present technology.

[1] Petroleum engineer, Division of Petroleum.
[2] Chemical engineer, Division of Petroleum.
[3] Barrels as used in this chapter refer to a 42-gallon barrel.

As new field and laboratory research data become available, a better understanding of the mechanisms, applications, and limitations of techniques will be developed. When performance of new processes can be predicted as accurately as that of present conventional methods, commercial application may be feasible. One effect may be that additional oil is recovered thereby at lower cost than by exploration for new reserves. Among the new innovations for oil recovery receiving attention are several methods to supplement waterflooding, which now is the predominant method used in secondary recovery.

One main reason that real drilling costs have been increasing is the greater depth of productive wells. Individual segments of drilling costs have increased only slightly; but as wells go deeper, their cost is greater. The industry is confronted with larger exploration expenditures, which in part have contributed to the long upward trend in real costs of finding domestic crude oil; but the major consideration in these costs is that most of the new discoveries are small oil and gas accumulations, and consequently the industry is paying more to discover less.

The economics of finding, developing, and producing oil that will provide domestic petroleum availability is of prime importance in the dynamic mix between consumer preference and the technologies of processing, use, and production so that the Nation may be certain that its ever-changing fuel needs will be met.

BACKGROUND

Petroleum, natural gas, and related bituminous materials have been used by mankind since antiquity. In the ancient world, pitch or native asphalt was used as a binder for pavements, for waterproofing cisterns, calking ships and grain silos, and for mummification. It is believed that the fires of the ancient oracles probably were burning natural gas seeps. North American Indians used petroleum obtained from springs for a variety of medicinal unguents, salves, and hair pomades, and for other purposes such as softening and waterproofing leather. In colonial times "rock oil" was a high priced and valued patent medicine about which great claims were made for a variety of medicinal purposes.

The first recorded production of natural gas in the United States was in western New York in 1821 when a gas seep on the banks of Canadaway Creek was ignited accidentally, demonstrating that natural gas was an excellent fuel. As a result, a well was drilled to a depth of 27 feet, and the gas was used for lighting. The delay in developing natural gas was due to economic conditions and limited technology, not neglect. Natural gas usually was found at locations remote from cities and therefore it was cheaper to serve city markets with gas manufactured locally from coal.

The modern petroleum industry dates from E. L. Drake's well which was drilled near Titusville, Pa., specifically in search for oil. Oil was found at a depth of less than 70 feet on August 27, 1859. At that time, there was a demand for a better and cheaper lamp oil. Whale oil was expensive, in limited supply, and unsatisfactory in other ways. Kerosine—as the name was coined originally—from coal and oil shale and generally called "coal oil," was made in about three dozen refineries in the United States at the time of Drake's well, but this product, too, was expensive and of poor quality as a lamp fuel. Some illuminating oil was being distilled from petroleum obtained from oil springs and seeps. In addition to lamp oils, there also was a strong demand for better quality lubricants.

The oil search spread to other States and countries. Ohio had very little production in 1860, but by 1876 had sustained output. West Virginia, Tennessee, Kentucky, Colorado, and California were producing small amounts of oil in 1865, and before 1900 were joined by Indiana, Illinois, and Texas. By them, oil was being produced in Rumania, Canada, Russia, Poland, Italy, Germany, Japan, Indonesia, Burma, India, Pakistan, and Peru. During this same period, Pennsylvania was the leading gas-producing State, and natural gas had been discovered in 17 States.

The first production in Mexico was in 1901. The great Middle East oilfields were slow to develop; the first oil was produced in Iran in 1913; 14 years later oil was discovered in Iraq. About two decades later the immense Bahrain and Saudi Arabian fields were discovered, followed by discoveries in Kuwait in 1946. The African Sahara's great potential was not proved until large new discoveries were made there in 1958, and important discoveries continue there even now. Venezuelan oil possibilities were first shown in 1917, and for many years it has ranked second to the United States in production in the Western Hemisphere. The United States, long an exporter of both crude oil and products, became a net importer in 1948, and imports of Venezuelan and other foreign oils and residual stocks gradually have increased. In 1963, 20 percent of the U.S. crude-oil supply

was imported. The Middle East now supplies the principal part of the rapidly expanding European market as well as the markets of several countries in the Eastern Hemisphere.

The first oil pipeline to transport crude petroleum satisfactorily in the United States was completed by Samuel Van Syckle of Titusville, Pa., in 1865. The line connected Miller's farm to Pithole City, about 5 miles away. Sections of 2-inch pipe were joined by fitted screw sockets. The line had 2 pump stations and carried about 80 barrels of oil per day. In 1872, the first iron pipeline was constructed to transport waste gas from nearby oil wells to Titusville, Pa. The 2-inch line was 5½ miles long and capable of delivering 4 million cubic feet of gas per day to 250 domestic and industrial customers.

A rapid buildup of large-diameter, long-distance pipelines for natural gas distribution began in the late 1920's when pipe-welding methods were perfected. Since World War II, many product pipelines for finished products, LPG, and petrochemicals also have been built, and the trend is continuing.

The first oil tanker was the SS *Charles* of Antwerp, Belgium, which sailed between the United States and Europe from 1869 to 1872. The ship had 59 iron tanks in its hold with a total capacity of 714 tons (about 5,000 barrels). In 1879, the first tank steamer was constructed by Nobel Bros., the pioneering petroleum refiners in Russia.

The internal-combustion engine, using both the diesel and Otto cycles, came into use in large numbers after 1900. This engine changed the oil industry because of the large gasoline market that developed to supply fuel for automobiles, trucks, and buses.

The first plant for extracting natural gasoline from natural gas by the compression and cooling method was constructed at Titusville, Pa., in 1904. At present, natural gasoline extraction is a large industry, and most gasolines contain some of this product which is used as an ingredient to adjust vapor pressure, boiling range, volatility, and octane-number rating.

For 50 years gasoline has been the major petroleum product. The spreading use of electric lighting had only a slight effect on the oil industry, because the increased demand for gasoline and other products offset the decreased usage of kerosine lamps, fuel for which formerly had been the major oil product market.

After World War I, the development and use of automatic burners for homes and industrial buildings resulted in increased consumption of oil fuels. In the past 20 years railroads have converted almost completely from steam to diesel locomotives because of greatly reduced costs for fuel, operation, and maintenance.

About 1930, the natural gas industry emerged as an essential dynamic industry because of the following factors: (1) the development of steel pipe at reasonable costs that was capable of withstanding great pressure for the transportation of gas over long distances; (2) development of more modern technology for exploratory work; (3) the rapid increase in demand for natural gas service because of its advantages as a clean, flexible, relatively low-cost fuel.

Continuous-distillation units were installed in refineries about 1900, but the conversion from batch to continuous stills was gradual. Large numbers of automobiles and trucks soon upset the refinery-product balances, because straight-run gasoline comprised only about 15 to 20 percent of the crude oil, and markets for the other products grew but slowly; consequently the non-gasoline fractions were in excess supply. Introduction in 1912 of the Burton thermal cracking process, which cracked gas oils, helped to solve this problem by increasing gasoline recoveries to 35 percent of the crude oil processed. Beginning in 1923, tetraethyl lead was used as a gasoline additive to increase the octane rating of gasoline and was a big factor in solving the "knock" problem in high-compression engines. It permitted greater use of lower quality gasolines and more efficient and higher performance engines.

Special aviation gasoline was necessary in World War I, and its composition, manufacture, and testing were greatly advanced in the 1920's and 1930's. A method to produce better quality gasolines was catalytic cracking which came into use in the late 1930's. Equally important was the development of several alkylation, polymerization, and related processes for transforming gaseous and liquid hydrocarbons into gasoline having high antiknock ratings. More recently new catalytic re-forming and hydrogenation processes have been developed, based on the use of platinum and other noble metals and various minerals as the active catalytic agent. This technology has made great transformations in the industry, both in gasoline manufacture and in production of a whole gamut of petrochemical, raw, intermediate, and fininshed products.

Soon after World War II, secondary-recovery methods came into use, and from 1930 to 1945 production obtained by using secondary methods, chiefly waterflooding, remained stable at about 20 million barrels of oil per year. After 1945, production from waterflooding increased at a very rapid rate. In 1963, production from secondary methods exceeded 800 million barrels.

Natural gasoline plants and refineries extract the volatile hydrocarbons, propane and butane, which are associated with petroleum and gas. These can be used in motor fuel only in small quantities because of their volatility, so until fairly recently they were not commonly used except as on-site boiler, furnace, or stationary engine fuel. Propane and butane are excellent heating fuels in the gaseous state, but they must be recovered, stored, transported, and utilized under pressure. Because of this volatility, the development of a substantial LPG industry awaited techniques, procedures, and equipment for extraction and utilization that were efficient, safe, and low in cost. Within the past 30 years the industry has grown phenomenally, chiefly because LPG components are major raw materials used for the manufacture of petrochemicals.

SIZE AND ORGANIZATION OF THE INDUSTRY

Petroleum

Petroleum products are readily available in every locality in the United States and in most countries throughout the world. In 1963, world crude-oil production was 9.5 billion barrels, of which the United States produced 29 percent, or 2.8 billion barrels. Domestic crude oil production, 7.5 million barrels per day, was 70 percent of the U.S. supply of which natural gas liquids supplied 10 percent. The remainder, consisting of crude oil and products, was imported.

The petroleum industry by its nature functions roughly in the following four groups: (1) exploration, drilling, and production; (2) transportation; (3) refining and processing; and (4) distributing and marketing raw, finished, or intermediate products.

In the United States and Canada the industry differs from that in the rest of the world largely because the free enterprise system allows individuals, small companies, and large companies to compete in all phases of the industry. There also is a large measure of cooperation between the various companies, some large, some small. State ownership of land and minerals is generally the case in most of the world outside the United States. This precludes any but the larger companies engaging in foreign operation in most segments of the industry. Many domestic companies (predominantly large corporations) have oil interests in other countries of the free world in production, transportation, refining, and marketing.

More than 18,000 operators are engaged in oil and gas exploration, drilling, and production operations in the United States. These include all legal entities, such as individuals, partnerships, corporations, subsidiary companies of integrated large corporations, and contract services (*4*).[4] Petroleum employment in the producing, recovery, and refining sections of the industry in 1963 was over 480,000 employees (*6*). Refinery capacities of the domestic units ranged from 1,000 barrels to 250,000 barrels daily, with a total daily throughput of almost 10 million barrels. Combined world crude oil refining capacity in 1963 was 250 million barrels daily in 627 operating refineries.

Natural Gas

Natural gas is the most rapidly growing of all the fuel energy resources in the United States and represents the sixth largest industry in the Nation in terms of investment. The 14.7 trillion cubic feet of marketed production in 1963 was a record output which increased 6 percent over the previous year and per capita gas consumption reached a record high of 78 million Btu, a gain of 33 percent in the past decade (*1*). Within the next 4-year period, 1964–67, the gas industry is expected to spend $7.2 billion on construction. During 1960–63 the gas industry spent $6.7 billion on construction, and $273 million for underground gas storage.

The natural gas industry comprises three interdependent branches: (1) producers, (2) pipeline companies, and (3) distribution companies. Some parts of the industry are regulated by National, State, and local governments to maintain an equitable relationship for consumers, industry, and investor.

The term "natural gas producer" includes the following functions: Exploration for finding, developing, producing, gathering, processing, and selling natural gas in the field. Most of the Nation's natural gas is produced by companies that do not combine producing with normal pipeline and distribution operations.

The main purpose of gas pipeline companies is to provide the essential linking of transportation from the producer to the distributor. A pipeline company must obtain a steady and reliable supply of gas and then deliver and sell it to distributors or directly to consumers, often under differing situations. Usually numerous producers are involved, and a variety of conditions prevail concerning price, location, and volume. Therefore, coordination of supply to match demand and to maintain an overall eco-

[4] Italicized number in parentheses refer to the items in the list of references at the end of this chapter.

nomic balance is essential to the gas pipeline company. Gas imports from Canada now have reached about 1 billion cubic feet per day and imports from Mexico about 135 million cubic feet daily. Exports to Canada are approximately 19 million cubic feet per day and those to Mexico, 27 million.

The gas distribution company usually is the only branch of the gas industry that deals directly with the consuming public, but some pipeline companies as well as some gas producers sell gas directly to large industrial consumers. The typical user of gas, whether residential, commercial, or industrial, normally depends on a distribution company as his supplier of gas service. In 1963, large volumes of gas were shipped from gasfields in 33 States through 710,000 miles of transmission and distribution lines to consumers in 47 States, leaving only Maine, Hawaii, and Vermont without gas service.

Interrelations Between Petroleum and Natural-Gas Industries

In most producing areas petroleum and natural gas companies engage in the same activities because oil and gas occur together in petroleum reservoirs. Elsewhere, these industries compete vigorously for the same fuel markets, in domestic and commercial heating, power generation, and industrial fuels.

An oil company often produces natural gas in quantity along with crude petroleum, and oil operators sometimes own "dry" gas wells (produce gas and no oil). Natural-gas companies buy gas from both sources. Conversely, natural-gas producers may own oil wells and sell their production to oil companies.

Most natural-gasoline plants are operated by the producing departments of oil companies, but some are operated by the producing or pipeline departments of gas companies. Others belong to companies that specialize in natural gasoline.

Interstate oil pipelines by law are common carriers and, therefore, are subject to Interstate Commerce Commission regulations. Natural-gas pipelines engaged in interstate business are subject to regulation by the Federal Power Commission. Gas pipeline companies contract to supply certain volumes of gas to their customers, including the local distribution utilities. Some contractual commitments are required before the Federal Power Commission will issue a certificate of necessity to build a gas pipeline. These commitments prevent the gas pipelines from being considered as common carriers as are railroads and oil pipelines.

Geographic Distribution of the Industry

In the past the natural-gas industry was forced to operate on a strictly local basis, but today the enormous and rapidly growing needs for energy outside North America suggest that gas will take its place alongside oil and be of comparable importance in major energy markets. In 1960, the accessibility of gas to European consumers was advanced by the discovery in the Netherlands of what has since proved to be the second largest natural gas field in the world. The Groningen discoveries in the Netherlands, within 375 miles of Paris and 125 miles of the Ruhr, have helped decrease the high transportation costs that have plagued the natural gas industry and have given gas substantially lower flexibility than oil in European markets. At the same time, the Groningen discoveries have been made more significant by the demonstration that marine shipment of natural gas, at atmospheric pressure but liquefied by lowering the temperature below −258° F, is technically feasible. This has made it practical for gas to supply markets too remote to justify the laying of a pipeline. Shipments of liquefied methane in specially constructed tankers from North Africa to France have already begun.

U.S. companies have a dominant interest in oil production in other areas of the free world, as well as in transporation, refining, and marketing. United States is the leading consumer and producer of oil. Within the past decade the United States has had a decreasing proportion of world production and use; however, in many other countries during this period, supply and demand for oil have had a higher growth rate.

The six largest oil-producing States are Texas, Louisiana, California, Oklahoma, Wyoming, and New Mexico. Each produced over 100 million barrels in 1963; the largest producer was Texas with 973 million barrels. For total natural gas withdraw output, the order was the same except that Oklahoma ranked third and California fourth. Principal gas-consuming States are, according to rank, Texas, California, Louisiana, Ohio, Illinois, Pennsylvania, and New York.

The preferred location for refineries combines several features, such as being on or near seaboards and producing areas, or both, and close to large markets and ocean transport. Good examples are the refining centers in the East on the Delaware River close to Philadelphia and New York; those on the gulf coast near Houston, Beaumont, and Port Arthur; those on the west coast near Los Angeles, San Francisco, and on Puget Sound, Wash. Inland,

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the largest refineries are in the Chicago and St. Louis areas.

The same pattern of location was followed in the great postwar refinery construction in Western Europe, the Middle East, and Venezuela. In the Caribbean, Aruba and Trinidad are the major refining centers. In the Middle East the principal refineries are in Kuwait, Bahrain, Ras Tanura, Saudi Arabia, Abadan, and Iraq, all of which are on the Persian Gulf.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

The petroleum industry's primary raw material—crude oil—has widely varying properties. Historically, crude oil has been sold on the basis of gravity. The higher API gravity oils contain more of the more valuable products, gasoline and light distillates, than heavier oils, so that lighter crudes sell at higher prices. Another criterion has been the amount of sulfur present. Many sulfur compounds have disagreeable odors, are toxic, and corrosive; oils containing them (sour oils) are more expensive to handle and refine, so they are penalized in the market. Other factors that reduce quality are salt and substances that poison cracking and reforming catalysts (in addition to sulfur), such as nitrogen compounds, arsenic, vanadium, and other minerals, and metals. Elaborate price scales for crude oils, which take into account both quality and location, have been established all over the world.

For natural gas the quality problem is simplified because its composition is less complex. The final product reaching the consumer is rather uniform in composition and heating value which usually is between 900 and 1,000 Btu per cubic foot. There is an increasing trend toward the sale of natural gas on a heating-value basis (therm, 100,000 Btu) rather than on a volume basis.

In the United States the major petroleum products are motor and aviation gasoline, and domestic and industrial fuels. Motor gasolines are sold in two principal standard grades by most refiners, three by others, and by a few companies in a series of grades blended at the service station pumps on an octane-number basis. There are five grades of aviation gasolines and three grades of jet-propulsion fuels. There are three standard diesel fuels and five standard grades of fuel oil. Lubricating oils, greases, and related specialty products have appropriate standards, and these products are produced in great number and variety to suit thousands of different needs.

Natural gasoline and LPG are petroleum products, but in the pactice of industry they are treated more as natural gas rather than petroleum materials. They, likewise, are sold in a number of grades for many purposes. Volatility is important in gasoline, and these volatile natural gasolines are blended into gasolines to give them the proper temperature-boiling range-vapor pressure properties to suit the type and location of use. Volatility of motor gasolines, for example, is varied in this manner as may be required by the season as well as the latitude and altitude.

The term "natural gas" is applied to all varieties of gases produced from underground rocks in which the paraffin series of hydrocarbons predominates. Normally the gaseous hydrocarbons in commercial natural gas are predominately methane (CH_4) with significant quantities of ethane (C_2H_6), with other hydrocarbons in small amounts. Natural gases, as produced, usually have small amounts of moisture, nitrogen, carbon dioxide, and hydrogen sulfide, and there also may be small percentages of helium and traces of oxygen, argon, and hydrogen. In a few locations, gas with a high carbon dioxide content is processed to manufacture dry ice or liquid CO_2. Sulfur compounds in natural gas-hydrogen sulfide and mercaptans are odoriferous, corrosive, and/or toxic impurities that must be reduced, altered, or removed for the gas to be suitable for domestic or commercial use. Gas companies in recent years have placed a minimum limitation of 20 grains of total sulfur and 1 grain of hydrogen sulfide per 1,000 cubic feet (Mcf) on gas for it to be acceptable for transmission.

TECHNOLOGY

The modern petroleum and natural-gas industry grew from a realization of the value of both crude oil and natural gas. The utility of natural gas was known and commercially exploited in the United States long before Colonel Drake "drilled the first oil well" in 1859. Drake's well was drilled directly as a result of Professor Silliman's scientific examination of a crude oil sample and his detailed report of the many useful and needed products that could be obtained from petroleum in quantity. Then little technologic skill was needed except the elementary skills of the brine-well drillers borrowed from the salt industry and those of the refiners borrowed from the coal-oil plants, which were striving to supply the illuminating-oil deficiencies caused by declining catches of sperm whales. Creekology and surface seeps were the methods used by the oil finder when Drake spotted his well location on an oil seep. The application of geology to finding oil began 25 years later when several fields were discovered,

based on the theory that oil accumulates underground in the crest of rock-layer folds, called anticlines.

The first drillers sought oil in places where oil escaped to the surface, and because seepages were found along streambeds and in low spots, wells were drilled in valleys. As the more venturesome drillers, the first wildcatters, found oil by drilling on hilltops away from oil seepages, and learned that oil existed thus without surface indication, it was realized that underground rock formations were more important than seeps when exploring for petroleum.

In 1848, before the Drake well, Sir William Logan, Director of the Geological Survey of Canada, visited the oil seeps of the Gaspé Peninsula and reported that they were on anticlines. This theory was not accepted in Pennsylvania for the simple reason that it did not apply in that State, which for over 50 years was the foremost oil-producing area in the world. Even in southwestern Pennsylvania and West Virginia, where large closed anticlines are found, oil occurs in lenticular sands and is as likely to be located off an anticline as upon it. The age of seepage drilling (that is, the location of wells near seeps) persisted far into the 20th century. The 1912 discovery of the Cushing field, Oklahoma, was the first attributed to the Federal Geological Survey. The period from 1912 to 1925, during which most of the principal anticlines in the United States were discovered, is therefore known as the "anticlinal" period. The end of this period is said to mark the initiation of modern scientific exploration.

Exploration

Early oil exploration was mainly a search for surface features which might indicate subsurface structures containing oil and gas. Few engineers or geologists were present in the early years of the oil industry, and it was only after they had been employed in numbers for a substantial period that knowledge was gained and used by the industry. Gradually conditions such as favorable source beds, marine environments during sedimentation, porus reservoir rocks, and tight gas-capped rocks were determined to be important for location of oil reservoirs. Driller's logs or other data on the underground rocks were put to use by the geologist for subsurface studies.

Today, petroleum engineers and geologists are constantly searching for new tools for interpretation of subsurface conditions. Some of the developments are electrical logging (resistivity and self-potential measurements of formations adjacent to well bores), microcaliper logging of holes and subsurface dip instruments, sidewall coring of boreholes, and electrically fired, explosive-propelled corebarrels. In recent years various types of radioactive well logging have been developed in the form of gamma ray and neutron instrumentation.

Perhaps the most useful instrument for geophysical oil prospecting employs shock waves and is known as reflection seismography. Seismographs have long been used to measure and record earthquakes. The instrument is so sensitive it can measure the footfall of an ant, and it is used to detect and record shock or sound waves reflected from subterranean rock strata. The shock wave is created by exploding dynamite or by generating seismic waves by dropping heavy weights on the surface (the "vibroseis" technique). When using explosives, a hole is drilled some 50 feet deep into the area to be explored and 5 to 50 pounds of dynamite are tamped into the hole. Shock waves are sent into the earth from the explosion or heavy impacts of waves just above or below the surface. The waves return to the surface either by reflection from subsurface interfaces or by refraction along them. These methods are expensive and are used only for detail work in favorable areas and sometimes where overall indications appear good for regional reconnaissance.

The trend toward higher cost of seismic operations will continue. Recently introduced refinements, such as magnetic-tape recording, transistor electronics, and high-speed automatic computers, combined with application of data-processing techniques, have improved the effectiveness of seismic operations; however, these refinements have also increased costs.

The gravity meter is used to explore underground structures by measuring the earth's gravity. It is essentially a sensitive spring balance which measures differences in the pull of gravity at different locations. A dense rock buried in lighter rocks will be indicated on the gravity meter by an increase in the value of the earth's gravity at points above the rock. The gravity meter is particularly useful in locating salt domes and salt beds because of the difference between the density of the salt and the other surrounding rock. Gravity meter surveys have located many salt domes in the Gulf of Mexico and adjacent gulf coast area, as well as a number of salt beds in Canada.

Geophysical prospecting also is done with a magnetometer, an instrument that measures the earth's magnetic field. Magnetometers are used chiefly in hard rock or in nonsedimentary areas to prospect for minerals. Like the gravity meter, they can be used to plot the contours of hard rocks underlying sedimentary rocks.

Essentially the instrument is a vertically mounted magnetic needle which measures the downward pull of the earth's magnet field. Rocks have varying degrees of magnetic attraction due to their orientation relative to the earth's magnetic field and their nearness to the earth's surface. Variation in readings of the magnetometer obtained over an area may be interpreted as indicative of the presence or absence of oil traps.

Gravimetric and particularly seismic methods have received added significance with the increasing interest shown since the late 1940's in those sections of the Continental Shelf which are submerged parts of potential oil basins. Special techniques have been developed to enable surveys to be conducted in the shallow seas covering such regions. Gravimetric instruments are lowered to the sea bottom on a cable, and the instruments are carefully leveled and adjusted by remote control before readings are taken. Several seismology methods have been developed which allow progress at sea much faster than on land. Marine geophysical activity has been most intense in the gulf coast area of Louisiana and Texas where the discovery of several oil-bearing or gas-bearing structures has amply proved the value of geophysical methods.

Neither geophysical nor geological surveys indicate the actual presence of oil. At the very most they can suggest the existence of an underground structure which may be favorable to oil accumulation. Only the drill can prove the presence of oil.

The soil-gas method is the best known geochemical technique for petroleum exploration in the United States. In using this technique, samples of the soil are gathered at intervals over the study area in a grid or profile pattern in search for hydrocarbon anomalies. The resulting data are plotted on a map which, if positive, reveal a characteristic "halo" effect. These anomalies do not give the nature (oil or gas) or the depth of the hydrocarbon source formation because the haloes are essentially static phenomena representing hydrocarbons locked in the soil from source oil or gas deposits. These hydrocarbons may or may not have migrated elsewhere.

Claims for the effectiveness of soil gas analysis are difficult to evaluate. Although such techniques have not proved successful in this country, the Soviets document numerous successes, the validity of which remains in doubt.

Drilling

Well drilling is a combination of art and science. In recent years the trend is toward more science and technology. The art of well drilling is very old and was practiced by the Chinese in drilling brine wells as early as 221 B.C. Their equipment was of the percussion type, although wells were drilled as deep as 3,500 feet in search of petroleum. Wells were drilled with a heavy tool called a bit, which hung from a rope and was jerked up and down by relays of men bouncing on a springboard. The weight of the periodically rising and falling bit drove it deeper and deeper into the ground.

In cable-tool drilling (sometimes referred to as percussion or churn drilling), the formation is pounded by a heavy bit on the end of a cable which is raised and dropped by machinery to produce a regular eccentric motion similar to the hand drill of the stonemason. The cable tool assembly is about 40 feet long and has four parts made of steel: The bit (about 6 feet in length), a long drill stem (a 25-foot cylindrical bar to add weight), jars (massive telescoping links to accentuate the motion), and a socket for attaching the cable. Weight on the end of a flexible cable (steel, formerly manila) causes the bit to strike the bottom of the hole with great force and break the rock.

Drilling is done with water in the hole so that the broken material becomes a slurry which periodically is removed from the bottom of the hole by pulling out the drilling tools and lowering and withdrawing a bailer on another cable. Cable-tool rigs are driven by steam engines, internal combustion engines, or electric motors. Steel pipe (casing) usually is screwed together as it is lowered into the well to line the hole. It prevents caving and is used to control ingress or egress of fluids (oil, gas, mud, and water) to or from the well in the various formations penetrated. The term "rig" includes a derrick or mast with the necessary hoisting equipment for spooling the various cables and a walking beam to raise and drop the drilling string.

At the turn of the century a radically different drilling system, the rotary method, was introduced successfully when drilling the discovery well of the famous Spindletop field, in the gulf coast region of Texas. No reciprocating movement is employed. A column composed of joints of pipe screwed together (termed a drilling string) is suspended by hoisting gear in a derrick. This string is turned by an engine which drives the rotary table and the hoisting equipment. The bit is screwed to the bottom of the column of pipe. Lowering of the drilling string is controlled so as to allow the desired amount of weight to rest on the revolving bit, causing it to penetrate the formation as it turns. The rotary bit bores a hole in the earth by slicing, crunching, or abrading the rock at the bottom of the hole. A stream of liquid, generally colloidal mud, is pumped through the drill

pipe, the function of which is to wash away the formation cuttings and bring them to the surface. The mud passes through nozzles or eyes in the bit and returns to the surface in the annular space outside the drill string. Holes can be made much faster by rotary drilling than by cable tool drilling, especially in the softer formations. Even so, a long time elapsed before rotary drilling obtained its present prominent place. Rotary rigs are relatively more expensive and require more men to operate. Cable tool footage is, as a rule, higher than rotary rig footage, but daily operating costs are lower, an important factor to small operators. The rotary system basically has remained unchanged since the Spindletop days. However, there is little resemblance between the rig of 1900 with its wooden derrick and a primitive hoist driven by a small steam engine and a modern rotary rig equipped with a steel derrick, pneumatic and hydraulic controls, and a group of gas or diesel engines to supply power having an output of 3,000 horsepower or more.

Water-base muds are employed extensively in drilling wells as the natural result of availability, low cost, and generally satisfactory performance. Oil-base muds and water-oil emulsion muds are often used, where damage may be done by contact of water with reservoir beds containing reactive clays. Aerated muds, oil, or air and natural gas alone may be used as the circulating fluid for relatively low-pressure exposure of producing formations when damage by excessive pressures might otherwise be incurred in these formations.

Advanced engineering has produced highly integrated units which can be speedily moved and erected. Drilling techniques, drilling fluids, and methods of identifying and evaluating the formations penetrated have been and still are being greatly improved. Rotary drilling is more costly per day than cable tool drilling, but it is about 10 times faster and more economical, particularly for deep drilling. Economy is an important consideration since most wells drilled today are over 5,000 feet deep, many are 10,000 feet, and a few have reached 20,000 feet. The deepest well to date is 25,515 feet. Since rotary drilling is the only method of reaching these great depths, almost 90 percent of drilled footage today is by rotary.

Marine Drilling

Before World War II, little effort had been given to drilling for oil in the underwater regions of the oil basins. In 1880, shallow wells were drilled from piers off the coast of Southern California near Ricon. In the 1920's, development of portions of the famous Lake Maracaibo, Venezuela oil field, and the offshore area of the Huntington Beach-California field, were drilled by means of directional wells drilled from beach locations. Drilling in the Caspian Sea near Baku was still a later development.

After World War II, intensified search for oil and favorable prospects in the Gulf of Mexico soon led to the drilling of the first offshore well. Since then, the technique of offshore drilling has developed rapidly, and many types of drilling platforms suitable for operations far from shore have been constructed. These are now designed for drilling in waters of varying depths up to several hundred feet, and wells are being drilled offshore in the Gulf of Mexico along the coast of Louisiana, Texas, and California.

Offshore work outside the United States is being done in scattered locations from the Persian Gulf to British Isles and from the Far East to the Caribbean area. The industry has not standardized on any particular style of rig for particular types of jobs, and rigs now putting to sea for the first time resemble each other as little as did the previous rigs.

Offshore drilling platforms are classed in three general categories. One of these fixed-derrick platforms are units large enough to carry derrick, drawworks, and engines erected on piles driven into the seabed. A seaworthy drilling tender is moored to the platform and contains the circulation pumps (connected to the platform by hoses), storage tanks for mud, drill pipe racks, casing, cement and cementing equipment, crew living quarters, and generally, a helicopter landing platform. The tender platform is a relatively deep-water tool, designed for operations in waters of 300 feet or deeper.

Self-contained platforms are best suited for development of a proved area. Such a platform does not require a tender and is particularly suitable for drilling a number of directional-deviated development wells. After completion of wells, the platform provides an area for the installation of production equipment such as oil tanks and pumps for transferring oil production into barges or, via a submarine pipeline, to a shore installation. A self-contained platform is designed for development operations in water to a depth of 110 feet.

Floating-mobile platforms are used for drilling exploratory wells because their mobility allows quick and comparatively inexpensive moves from well sites. Producers use this method to move in, evaluate a lease with test drilling, and move out rapidly at minimum expense. The mobile unit includes space for drilling equipment, a helicopter port, mud tanks, pipe racks, crew quarters, communications,

cooking and recreation facilities, auxiliary power, and other miscellaneous equipment. Such built-in flexibility enables a company to drill vertical holes which are 50 percent cheaper than deviated holes from a fixed platform. The ability to move to different locations diminishes the danger of a blowout destroying a cluster of wells, as is the case on multiple well permanent platforms. Since all equipment is on the platform, downtime (time when drilling operations ceases) resulting from wave action is reduced. The water depth limitation for floating mobile units is now about 125 feet.

Many oil prospects in soft, marshy soil on the gulf coast of Louisiana and Texas are readily reached by shallow-dredged canals. Here a drilling unit is mounted on a large flat-bottomed barge which is divided into compartments. The barge has a narrow longitudinal slit in the hull from one end to the center under the derrick. The drilling barge is towed to the drilling site and is settled on the bottom by flooding the tanks. After a well has been completed, the barge is raised by pumping out the tanks and is floated off the well site. In general, such barges are capable of work in water depths to 80 feet. Barges of the submersible and self-elevating types continue to be popular for work within their depth ranges, and their depth capacity continues to increase.

Between 75 and 80 offshore units are now working in the waters of Louisiana. This includes 30 mobiles, 30 tenders, and the rest self-contained units.

Formation Evaluation

Drill stem testing, first developed over 35 years ago, is a method of evaluating the producing potential of a given horizon. The tests involve removing the hydrostatic pressure of the drilling fluid column from the formation and allowing formation fluids present to flow into the empty drill pipe. Data obtained include quantity and quality of produced fluids during a measured time interval. Such testing is the most reliable method known for evaluating a potential reservoir short of completing the well. Economics of the method are gained because the method eliminates the necessity of completing the well to test potentially productive formations.

Coring is a process of obtaining formation samples from the hole by special apparatus, or as drill cuttings returned from the formation face by the circulating drilling mud. Cores taken over the total depth interval of the prospective productive interval have the advantage of representing the reservoir as it occurs in the subsurface strata. Core data provide essential information concerning bed contacts, dip, grain size distribution, grain orientation, porosity and and permeability values.

Well logging may in some instances replace continuous coring, but it is generally used to supplement core data. At best, both methods can only infer the presence of oil or gas. Of the many existing logging tools, electric, gamma ray, neutron, and sonic logs are the most widely applied. Comparisons of the different logs enable determinations and estimations of geologic and reservoir data required for the ultimate technology in well completion practices and overall recovery of hydrocarbons.

Well Completion

Wells drilled for production of hydrocarbon fluids normally are walled or cased with one or several strings of tubular casing to protect fresh-water formations, to support the walls of the hole to prevent caving of the incompetent formation beds, and to protect produced hydrocarbons from contamination. A conventional well completion may involve the installation of two, three, or more strings of casing, "telescoping" within each other, with each string extending to a depth dictated by local formation conditions. Before casing is placed into the hole, the borehole may be reamed and scraped or acid treated to remove mud accumulations to improve cement bonding.

Oil-well cementing is the process of displacing cement slurry down the casing, tubing, or drill pipe to a predetermined point in the well. Cement is forced into the annular space between the casing and the wall of the hole and allowed to set and form a permanent barrier to the movement of fluids. More than half of the cement pumped in wells within the last two or three decades contained some type of additive. Over 30 special additives are available to change oil-well cements for specific applications.

Several choices of perforating equipment are available to provide the most useful path for flow of fluids into or from a cased borehole. Detonation of explosives in open hole opposite low-permeability sandstone formation is probably the earliest method of perforation used. The explosion creates fracture and fissure systems in the surrounding pay, and extends the wellbore. In conventional completions the formations are exposed by shooting holes at preselected intervals and densities over the length of the selected sections. Using a gun perforator, the holes through the casing and cement sheath are created by jet charges, or bullets. Following this exposure on a potential flowing well, tubing (usually of 2-inch internal diameter for single zone completion) is installed in

the well and attached to the casinghead. An assembly of valves and variable chokes are placed above a master valve on the tubing head, referred to as the "Christmas Tree." This assembly is arranged to direct the fluid flow from the well to lease facilities.

Acidization is frequently applied to acid-soluble carbonate reservoir rocks, such as limestone and dolomite, to open up or enlarge flow channels to the wellbore by dissolving barriers and restrictions in the formation. Hydrochloric acid is basically the main constituent because it is the most efficient and economical acid available for permeability improvement. Acids are modified in advance to suit the formation.

One of the most outstanding well stimulation methods for increasing well productivity is hydraulic fracturing. Many fields are in existence today because of these fracturing techniques for, without them, many producing horizons would very probably have been bypassed in the past 15 years as either barren or commercially nonproductive. Hydraulic fracturing of formations is produced by the application of sufficient hydraulic pressure to the face of the exposed subsurface productive formation to induce fractures in the formation. The technique is a means of increasing the effective permeability and is particularly applicable to formations with naturally low permeability. In thick producing sections, parts of the sections are isolated and fractured separately to insure maximum effectiveness.

The most common fracturing fluid used is lease oil. Although oil is not always the most satisfactory, it can be used more universally than other fluids. Fracturing fluids are classified into the following general groups: (1) fluids, (2) gels, and (3) emulsions. Fluids used are oils, fresh water, salt water or oilfield brines, and acids. Gels used are composed of oil, water, or acid with a proper chemical added to the base fluid to increase its viscosity. Emulsions are comprised of two fluid phases: (1) oil and (2) water or acid. They are formed by mixing the two phases together in correct proportions in the presence of an emulsifying agent to form either oil-in-water or water-in-oil emulsions.

In addition to fluids, the fracturing medium contains a propping agent to hold the fracture open to increase effective flow of formation fluids to the wellbore. Sand has been used almost universally for this purpose. Recently, glass pellets, aluminum pellets, nutshells, or plastics have been introduced as propping agents.

A permanent completion involves placing the lower end of the well tubing above one or more potential producing intervals and subsequently performing all completion and recompletion work with small tools that pass through the tubing. After the well casing has been set and cemented, this type completion can be used with any common size casing and tubing, provided the well is properly equipped.

Multiple completion is a technique which permits two or more reservoirs to be produced simultaneously, but separately through the same wellbore. Most multiple completions are used only for production. Many wells of this type serve as multiple injection wells for pressure maintenance or secondary recovery projects. Others are used for the injection of fluid into one or more reservoirs while maintaining production from others.

Recovery of Petroleum

Oil and gas accumulates underground in reservoirs of porous rock masses which have impermeable rock boundaries. In such a reservoir generally, free gas, if present, will occupy the space above the oil, and water, if present will occupy the space below the oil.

In any system fluids flow from regions of higher to lower pressure, and within a reservoir the flow is toward the producing wells. This movement is the result of: (1) propulsive action of gas either free or in solution in the oil which expands by lowered pressure to force the oil and gas through the pore spaces in the reservoir rocks; (2) displacement action of water from adjoining parts of the sand; and (3) gravity drainage. The space vacated by the removal of oil is filled by expansion and movement of the remaining oil, gas, and water. The general reservoir types are classed according to the major recovery mechanism.

(1) Gas-drive fields are reservoirs where oil accumulations are overlain by a gas cap. Movement of the oil results primarily from pressure of gas within the gas cap, supplemented by expanding gas liberated from solution in the oil. In this mechanism, the pressure reduction accompanying oil production allows the compressed gas in the gas cap to expand, to invade the oil zone downstructure, and to drive oil toward regions of reduced pressures at the producing wells. Under efficient operations a gas cap drive is capable of yielding approximately 20 to 60 percent of the original oil in place, depending on the size of the gas cap.

(2) Water-drive fields are reservoirs in which the space voided by the oil produced is refilled entirely or in part by water from the adjoining parts of the sand. No "free" gas is present in the reservoir as long as formation pressures are maintained above the saturation point; that

is, above the pressure at which gas comes out of solution from the oil. A small fraction of the space voided by the produced oil is taken up by the expansion of the oil plus dissolved gas still present in the reservoir. Water-drive fields are typified by slight or no declines in reservoir pressure with approximate recoveries between 30 to 80 percent of the original oil in place.

(3) Depletion reservoirs are those from which the oil is produced by gas liberated from solution in the oil, and aided by gravitational forces. Ultimately the available energy becomes inadequate to move oil, and some means of secondary recovery must be initiated. Oil recovery by depletion drive is basically and inherently inefficient, with the average recovery from about 10 to 25 percent of the oil in place in the reservoir.

Seldom do reservoirs produce by a single drive mechanism, but instead produce from several of the drives at sometime throughout the life of the field. For simplicity, a reservoir is classed by the dominant mechanism, although other drives may have some effects.

When reservoir pressures are high enough, wells will flow; that is, the oil and gas are produced because of natural energy latent within the fluids as they exist within the reservoir rock. In flowing wells this energy is utilized not only to expel the oil from the reservoir rocks into the well bore but also to lift it to the surface. Oil and gas may be allowed to flow to the surface through the casing, but usually the oil flow is confined within a smaller auxiliary column of pipe (tubing) suspended within the casing.

After natural flow stops, it is necessary to install additional equipment to lift the oil to the surface. Lifting methods fall into two general classes: (1) gas-lift methods and (2) mechanical pumping.

The "gas lift" method of producing oil (and water) involves the injection of natural gas from the surface through the space between the casing and tubing with resultant production of the gas and oil through the tubing.

The mechanical devices for lifting liquid in wells include the various types of oil-well pumps, of which rod-actuated plunger-displacement pumps and centrifugal pumps are the most common.

In the past, waterflooding has been applied on a large scale only in shallow oil sands but now is being applied in deeper reservoirs. A typical waterflood has an initial fillup period of several months before there is any marked pick-up in oil production. This initial period is usually followed by rapid increase in oil recovery, and combined fluid output continues thereafter with a gradual decrease of oil, and a corresponding water increase until the project reaches its economic limit.

After primary methods of extracting oil from reservoir rocks no longer recover oil at economical rates, many fields still are capable of yielding large quantities of oil economically by stimulative or secondary methods.

Hydrocrabon recovery can be increased by applying energy to maintain pressure or to move oil, gas, and related hydrocarbons through a reservoir by the injection of liquids or gases into the reservoir. Injection of gas and water into reservoirs has been practiced for the past 90 years to increase recovery.

Secondary recovery in early years was started when a reservoir was near its economic production limits. The growth in use and in the understanding of the technology and the economics of secondary recovery operations has led to the starting of more projects early in the productive life of the reservoir, and increased recoveries have been obtained. The majority of oilfields now are operated to obtain a maximum recovery of oil by maintaining a minimum change in reservoir pressure.

A number of experimental recovery methods are in various stages of tests in the laboratory and in the field. Miscible phase displacement has been thoroughly studied in the laboratory and has undergone field testing. The method consists of injection of alternate slugs of dry gas and water, or simultaneous injection of either dry gas and water, or enriched gas and water. The purpose of these types of drives is to improve the sweep efficiency in heterogeneous formations by the use of solvents that are miscible with the reservoir oil. Up to now, these methods have been promising, but not outstanding. Two other approaches being tried are based on methods for introducing heat into the reservoir. These are fireflooding, or in-situ combustion, and steam injection. Steam injection is the most popular new method because of its simplicity and fast payout. Both methods are directed to obtain additional recovery from deposits of heavy crude, previously considered uneconomic. Before these methods can be used with confidence, additional technology must be developed, for both have been used on a limited basis.

The high-pressure gas injection process has proved successful in reservoirs containing crude oils of 35° API gravity or higher. In this process natural gas is injected at pressures near 4,000 pounds per square inch to oil formations, which results in vaporization of the crude. Pressure maintenance or cycling operations are usually undertaken on gas-condensate reservoirs where insufficient water drive is available to

maintain the pressure in the producing interval at or above the dew or bubble point of the fluid.

Natural Gas and Natural Gas Liquids

Natural gas is produced by methods similar to those used in producing crude petroleum. The only differences result from the physical characteristics of the two commodities. Three types of reservoirs—dry gas, condensate, and oil—produce natural gas. Gas from dry-gas reservoirs is accompanied by only relatively small amounts of liquid hydrocarbons when it is reduced to atmospheric pressure and temperature. Gas from condensate reservoirs is accompanied by larger amounts of liquid hydrocarbons which may be in the gaseous state under reservoir conditions, but liquefied in the production and processing operation. Gas produced from oil reservoirs may be either "gas cap" gas from the crest of the reservoir or solution gas liberated from the oil as pressure and temperature are reduced in the production process. In the primary phase of producing a petroleum reservoir, the reservoir pressure gradually is reduced by producing the reservoir fluids (oil, water, and gas). The production rate normally exceeds the influx of water even in the most effective natural water drives, with the result that the reservoir pressure under these conditions also will decline unless the natural drive is supplemented by the injection of water or gas from the surface. As the reservoir pressure declines, a larger portion of the gas in the oil comes out of solution, thus resulting in higher produced gas-oil ratios. However, when the reservoir pressure is maintained, or permitted to decline only to a predetermined point through injection of water or gas, the produced gas-oil ratio will not exceed the solution gas-oil ratio until a breakthrough of injected gas or gas from a gas cap occurs.

In a gas-condensate reservoir the hydrocarbons originally are considered to be in a single gaseous phase at reservoir pressure and temperature. On reduction of pressure, condensation of some of the hydrocarbons will result. The liquid so obtained is termed "condensate." Condensation of the gas to form a liquid when pressure is reduced is a phenomenon directly opposite to common concepts. Normally when a substance is near the dewpoint, an increase in pressure results in condensation and a reduction in pressure causes evaporation. Gas-condensate reservoirs contain, in addition to the condensate, natural gasoline and lighter hydrocarbons similar to those found in gas associated with oil. The extractable constituents fall into the broad classification of natural-gas liquids; the amount ranges from 10 to 75 barrels per million cubic feet of gas. In the cycling process of producing gas-condensate reservoirs, the dry residue gas is returned to the reservoir, thus retarding condensation with resultant loss of liquids and preserving the dry residue gas for later marketing.

Extraction Processes

Methods of extracting hydrocarbon liquids from natural gas are the results of three stages of development. In the early years of the industry, extraction was accomplished by compression and cooling. The crude natural gasoline recovered by this method contained a substantial amount of butane and propane which made the gasoline unstable at atmospheric pressure and temperature. As the more volatile constituents vaporized, some of the desirable heavier components were carried with them. Because of the inefficiency of this method, the number of compression plants has declined, and they have been replaced by larger and more efficient absorption units.

The absorption process involves passing the produced gas through an absorber countercurrent to the absorption oil from which the liquefiable hydrocarbons are removed by distillation. The process gives high extraction efficiency and is capable of close operational control.

Petroleum Refining

The petroleum refining industry has blazed an impressive trail since the mid-19th century. Out of the small hand-tended batch stills and batch treaters of years ago have evolved the complex and highly automated refineries of today.

Today's refining plants are made up of multiple integrated processing units designed and operated for manufacturing with precision a multitude of finished or semifinished products from crude petroleum. Although the refineries are highly specialized in one sense, they are at the same time flexible enough to be adaptable to changing demands in quantity and quality of products. Such flexibility may on occasion be achieved by varying the type of crude oil that is charged. In other cases, changes in equipment or in process variables may be required. The petroleum refining industry, through continuous development, has continued to meet changing demands by the evolution of new processes involving steady progress in application of science, technology, and engineering.

Crude petroleum has few uses in the raw, unrefined state. It contains chiefly hydrocarbons, ranging from highly volatile compounds

to viscous fluids and heavier materials that cannot be distilled.

Distillation

Atmospheric distillation—the first process that was used for refining petroleum—remains the basic operation in modern refineries, but modern equipment and techniques are employed. It makes use of differences in boiling points of the constituents of the crude oil to separate it into many fractions which are the charge stocks for subsequent processes. The primary distillation unit operates at about atmospheric pressure. One or two separate fractionating columns may be used in this unit. The oil is heated by passing it through tubes installed in a gas- or oil-fired furnace, and vapors from the heated oil are then fed to the fractionating tower containing numerous trays.

Operation of the fractionating tower is countercurrent. The tower is hottest at the bottom, and each successive tray upward is at a lower temperature. As hot oil vapors rise, those having the higher boiling points condense on the lower trays and the lower boiling materials pass upward to condense on the upper trays, or pass on in the vapor state. The condensate flows down from tray to tray and serves to scrub the rising vapors to establish a vapor-liquid equilibrium at each level in the tower. Fractions having definite boiling ranges can be withdrawn constantly from the various trays and bottom of the tower (residuum) as liquids. Vapors from the tower top (overhead) are subsequently condensed to liquids by heat exchange. Noncondensed gases pass off with the overhead fractions. The residuum may be charged to a vacuum fractionator, sometimes termed a "secondary distillation unit", for additional separations, where, because of lower pressure, more of the oil may be vaporized below decomposition temperatures (about 800° F) than is possible at atmospheric pressure.

In the atmospheric column the products in general are, top to bottom: gasoline, kerosine, light gas oil, heavy gas oil, lubricating distillates, and residuum. These are continuously removed overhead and from drawoffs at specific trays down the column and from the bottom. The highest boiling material from the bottom of the column in some cases is reheated and fed to a vacuum distillation unit to separate the heavier distillate and residual lubricating oil stocks, residual fuels, and asphalts.

Practically all straight-run products from the distillation steps must undergo further refining that may include acid, caustic and solvent treating, dewaxing, decolorizing, blending plus addition of special additives. Those fractions that are not prepared as straight-run products undergo various cracking and other conversion processes discussed later. Each product during manufacture through the various steps must meet specifications of the buyer. Generally, marketed products are prepared to American Society for Testing and Materials or Government specifications.

Thermal Cracking

Thermal cracking was the first major advance in petroleum refining for obtaining more and better gasoline from crude petroleum than could be obtained straight run. It was introduced in 1913 and was the dominant processing feature of refineries for over three decades. Thermal cracking means the decomposition of oil by heat. The oil fractions are brought to about 950° to 1000° F and usually 250 to 300 pounds per square inch, with the result that the hydrocarbon molecules break apart, or "crack," to yield lighter products such as gases, gasoline, and naphtha, and heavier products such as cracked gas oils and asphalt and in the more severe thermal cracking processes, petroleum coke. Yields of gasoline from some crudes can be increased from about 15 to 50 percent or more by thermal cracking, and production of heavy residual fuel oils can be eliminated entirely through thermal coking.

Catalytic Cracking

As the knowledge grew of petroleum composition and its reactions under various conditions, it was learned that cracking could be done better and yield more and higher quality products if the cracking is done in the presence of certain solid mineral particles. These solids are known as catalysts and their use in refining is termed "catalytic," or "cat" cracking. The first commercial catalysts were specially treated bentonitic clays, but soon synthetic ones were developed which improve yields and operations. Catalyst particles are about one-sixth inch in diameter and usually are in the form either of pellets or beads. The active components usually are silica, magnesia, zirconia, and alumina, singly or in combinations. "Cat" units of large and small sizes have been built that charge from as low as 1,500 to over 60,000 barrels per day. Enormous amounts of catalysts are circulated through these plants, and in some the rate may be as high as 70 tons per minute. Operating pressures are low—10 to 30 pounds per square inch—and reactor temperatures are from 800° to 900° F.

Alkylation

Cracking processes also yield quantities of light hydrocarbons having two to four carbon atoms that have high octane numbers, but these

hydrocarbons are too volatile for blending into gasoline. However, they may be brought into chemical combination by catalytic alkylation to form compounds (alkylates) that have higher molecular weights, higher boiling ranges, high octane numbers, and are less volatile. From this alkylate mixture blending stocks are extracted for use as components in the best aviation and motor gasolines. The supply of alkylate at times during World War II was a limiting factor in producing aviation gasoline (avgas). Currently, much alkylate goes into motor gasoline, and it provides a substantial portion of the high-octane gasolines being sold. Nearly all alkylation processes employ either concentrated sulfuric acid or hydrofluoric acid as the catalytic agent, but some phosphoric acid is used.

Catalytic Reforming

During World War II, a large demand developed for aromatic hydrocarbons, mainly benzene and toluene, but also cumene (isopropyl benzene), styrene (phenyl ethylene), and other aromatics. Their traditional source was from the coking of coal but this supply was inadequate, and the petroleum industry began to supply an increasing share of the demand. Some aromatics were obtained by the petroleum refiners from various straight-run, cracked, and reformed naphthas, usually by the use of selective solvent and distillation processes.

Catalytic re-forming is a procedure for altering the molecules of straight-run or other naphthas. This method converts some nonaromatic constituents into products containing aromatic compounds. Their amount and nature depend upon the charge stock and conditions selected.

Following World War II, and especially during the Korean war, catalytic re-forming grew in use. Not only was this a means of producing aromatic compounds, but also as a source of high-octane gasoline in greater volume than was possible by methods formerly used. Much of this was due to the development of processes using platinum and other noble metals as well as various nonnoble metals and minerals as catalysts. Re-forming plays an important role in upgrading low-octane stocks to the demand for premium gasolines, and supplying aromatics to the rapidly expanding petrochemical industry. "Cat re-forming" is important for another reason—a large amount of byproduct hydrogen results from the chemical reaction of re-forming. This low-cost hydrogen has aided the rapid development of hydrogenation and processes involving hydrogen treating which are used for upgrading products, such as diesel and other distillate fuel oils and for improving storage stability, through desulfurizing, removing nitrogen, and for improving burning characteristics. Lubricants, various straight-run and cracked light and heavy gas oils, are hydrogenated as a step in preparing feedstocks for further processing. By these methods the refiner is able to produce more and better distillate products from crude petroleum and to reduce the amount of low-value "bottom of the barrel" heavy fuel oil. In the future, hydrogenation alone and in combinations with catalytic reforming, such as hydroforming, are expected to have increased use in upgrading refinery stocks which will accentuate the continued decline of heavy fuel production per barrel of crude.

Chemical Treatment

Low boiling fractions which occur naturally in petroleum and are separated by distillation with little or no decomposition generally are called "straight run" distillates. Included are gasoline, naphthas, kerosine, and gas oils. Fractions prepared in this way are distinguished from cracked products. It also is common to designate straight-run oils as "virgin" stocks.

Straight-run distillates contain mostly nonreactive compounds and usually require little chemical treatment. Cracked distillates require treatment because they have been subjected to severe temperatures and pressures and contain unstable, reactive compounds that form undesirable materials such as gums and color bodies. They also may contain various impurities such as nitrogen and sulfur compounds. These materials are removed or altered to improve the color, odor, stability, burning qualities, response to tetraethyl lead, and other properties of the products. Some lubricating-oil fractions require solvent extraction, dewaxing, acid and alkali treating, clay decolorizing and other processing, including hydrogenation which in some modern petroleum refinery technology is classed as treatment.

In early days of the refining industry, sulfuric acid was the principal chemical reagent used in treating petroleum fractions. Caustic soda solution and sodium plumbite (doctor solution) were next in importance. Sulfuric acid removes gum-forming compounds from light distillates and caustic soda removes hydrogen sulfide. Doctor solution converts odorous mercaptans to insoluble lead sulfide and odorless, oil-soluble disulfides. Many other processes for treating light distillates have been developed involving oxidation, catalysis, hydrogenation, and distillation and solvent extraction methods. Continuous methods generally are employed, but batch treating still is being used in many plants.

Solvent Refining

Solvent refining of lubricating oils has contributed markedly to petroleum utilization. In these processes a petroleum fraction is mixed with another liquid (or a combination of them) that is not completely miscible with oil, but has a preferential solubility for some of its constituents. The mixture upon settling separates into two layers: One is rich in the petroleum fraction which has been freed of undesired constituents (raffinate) but contains a small amount of dissolved solvent; the other layer is a mixture of undesired materials (extract) and is rich in solvent. The solvent is recovered from each of the two mixtures by distillation and is reused in the process. The raffinate oil has improved characteristics, such as low rate of change of viscosity with temperature (high viscosity index), increased stability, better color and appearance (bloom) and a lower carbon residue. Lubricating oils manufactured by solvent treating Mid-continent stocks of "mixed" base have characteristics similar to lubricants made from more paraffinic crudes.

Solvent refining is not new. A liquid sulfur dioxide process was used to extract aromatic constituents from Rumanian kerosine almost 50 years ago, but large-scale use of solvent refining for lubricating oils is relatively recent. A variety of solvents and mixtures of solvents is used for the major application of refining distillate and residual lubricating oils and waxes. The first commercial units for solvent-refining lubricating oils were installed in 1927. Approximately 70 commercial units for lubricants, waxes, and other oils are in operation in the United States.

Some solvent treating also is used to improve the lighter distillates: naphthas, kerosine, diesel fuel, burner oils, and catalytic cracking feed and cycle stocks. Treating solvents that are used singly, and in combination, include liquid sulfur dioxide, liquid propane (both of which require pressure at low temperature), furfural, phenol, and cresols.

In addition to solvent treating, there is a widely used solvent dewaxing process that uses a combination of aromatic solvents and refrigeration both for removing wax from oils (usually lubricants) and to deoil waxes. Waxes that are obtained are a valuable coproduct of lubricating oil manufacture. The solvent dewaxing process uses various mixtures of benzene and toluene with methyl-ethyl-ketone and/or acetone (di-methyl ketone). A common dewaxing solvent mixture is one part each of benzene, toluene, and ketone.

USES OF PETROLEUM, NATURAL GAS, AND PRODUCTS

The principal uses of petroleum are to produce heat and power. There is a diversity of fuels and heating equipment in most American cities. Natural gas and LPG are both burned for all forms of heating and compete with distillate fuels oils for space heating, especially for homes and small buildings. The larger oil-burning heating units in apartments, industrial and commercial plants, and electric utility stations that usually are fired with residual fuels or solid fuels frequently have natural gas as a standby fuel. Petroleum coke is burned in a few large utility furnaces and some is sold as briquets, but it is not a large volume fuel. Two other formerly important heating fuels are gasoline and kerosine, but heating units to burn them now are used only to a very limited extent.

Power for almost every kind of transportation on land, sea, or air is or can be supplied by burning petroleum fuels. Gasoline is available any place in the United States, nearby or within a few miles, as are light and heavy fuel oils. Railroads, buses, and trucks consume large amounts of diesel fuels. The volatile LPG fuels are used chiefly for space heating, but to an increasing extent they also are being burned for many types of transportation, including passenger cas, buses, and trucks. Most ships burn residual or diesel fuels and virtually every piece of machinery is lubricated with petroleum oils and greases.

The petroleum industry is organized for and depends on large-volume operations to be economically successful. Although there are over 5,000 petroleum products, about 90 percent of them are gasolines and fuel oils; the remainder includes such products as lubricants, solvents, wax, asphalt, coke, chemicals, petrochemicals, and a wide variety of specialty products. Substantial portions of the total supply of many important chemicals and commodities are oil based. Noteworthy are benzene and phenol which are two of the most important aromatic chemicals that formerly were obtained from coal tar, but the major supply of which now is petroleum based. Table 1 shows the 1963 refinery production of the major products which amounted to over 3,360 million barrels of products.

Gasoline

The largest use of gasoline is for spark-ignition engines in passenger cars, trucks, and aircraft. A large part of the total gasoline production contains natural gasoline as one of the ingredients blended with other stocks to produce

finished motor fuel. Chief among the components are straight run, thermally cracked, catalytically cracked naphthas, natural gas liquids (NGL), and various products from the more sophisticated catalytic processes such as polymerization, hydrogen treating, re-forming, and isomerization. To the blends also are added other agents such as antiknock compounds, deicers, antifouling additives, and dyes.

TABLE 1.—*Output of petroleum products at refineries in the United States in 1963*

Product:	Production, thousand barrels
Gasoline	1,603,304
Kerosine	164,705
Military-grade jet fuel	98,745
Distillate fuel oil	764,483
Lubricants	63,086
Wax	5,126
Residual fuel	276,766
Asphalt and road oil	118,740
Coke	80,628
Petrochemical feedstock	91,356
Miscellaneous	93,936
Total	3,360,875

Kerosine

In 1963, about 44 percent of the kerosine was consumed as commercial jet aircraft fuel. The remainder was consumed for illumination, heating and cooking, tractor fuel, and other minor uses.

Jet Fuel (Military Grade)

Most of the jet fuel listed in table 1 was used by the military. Military-grade JP–4 jet fuel is a wide-cut gasoline (approximately 65 percent gasoline and 35 percent kerosine materials) and the JP–5 grade is a high flashpoint kerosine. The components of blended jet fuels are low-volatile gasoline, naphthas, kerosine, and a small amount of other distillate fuels.

Distillate Fuel Oil

Refineries in the Texas Gulf Coast and East Coast Districts produced over 43 percent of the total 764.5 million barrels of distillate fuel oil in the United States in 1963. Total U.S. consumption of distillate fuel reached 748 million barrels in 1963 for a 2.6-percent increase over that of 1962. Heating oils, diesel fuel, and railroad fuels (includes diesel fuels) accounted for 70, 14, and 12 percent, respectively, of the distillate fuel oil consumption.

Lubricants and Wax

The 63 million barrels of lubricants produced in 1963 was less than 2 percent of refinery output, but this small proportion of the crude going to lubricants reflects several trends: Improved quality of all types of lubricating oils and greases that enables them to withstand harder and longer use; changes in engine and other equipment design that have reduced consumption; and a decline in exports caused by increased foreign lubricant manufacture. Lubricating oils usually contain different types of additives which are specially prepared to meet service conditions. It is not unusual, for example, for the additives in a lubricant to cost more than the petroleum oil present in it.

The demand for petroleum wax in 1963 was 5,264,000 barrels, a 2.4-percent decline. Domestic demand continued to decline, but exports were slightly higher than they were in 1962.

Residual Fuel Oil

The U.S. refinery output of residual declined 52,000 barrels daily in 1963, and represented 8.6 percent of the crude charge to stills which was a decline from 11.2 percent in 1960. The reduction of domestic residual oils output is indicative of the increased trend by refiners to coke low-value residual oils and to use of various hydrogenation and related processes to upgrade resulting cracked distillates. Thereby a larger proportion of the crude product yield is higher valued distillates. Imports of residual fuel, which are subject to quota regulations of the Oil Import Administration, amounted to an average daily total of 567,000 barrels in 1963.

Coke, Asphalt, and Road Oil

Asphalt and road oil have maintained an almost constant percentage yield position for the past 10 years at about 3.5 percent of crude oil processed. These products are playing an important role as paving and waterproofing materials in the Nation's road building and construction industries. The most important and growing nonfuel uses of petroleum coke are for metallurgical electrodes used in the aluminum industry and for electric motor brushes.

Petrochemicals

Petrochemicals are chemicals derived from petroleum and its products, LPG or natural gas. This definition is broad and there are no clear-cut lines of distinction between petrochemicals and organic chemicals from other sources. For example, synthetic fibers are considered to be petrochemicals in some cases, while in others they are considered to be chemicals.

The discovery by Carlton Ellis, in 1916, of a method to make isopropyl alcohol from propylene derived from petroleum sometimes is

called the beginning of the petrochemical industry. In the early part of the 20th century, coal tar, wood, and certain fermentation processes were the major sources of organic chemicals. Since then, petroleum has become increasingly important as a source of chemicals. The growth of the organic chemical industry can be attributed largely to the development of various treating, cracking, and re-forming processes, more efficient methods of fractional distillation in refining, and chemical synthesis. Most of these have been strongly influenced by the use of catalysts. Byproducts of many refining processes formerly used as refinery fuel or included where possible in marketed products now provide the raw materials used in the synthesis of organic chemicals.

The chemical industry is composed of many small and distinct industries which manufacture more than 10,000 commercial products. These range from simple basic raw materials, such as sulfuric acid, to complex hydrocarbon polymers and plastics that may be further processed to form films and fibers. Production of petrochemicals currently is approximately 30 million tons per year, double the 1955 production.

The oil industry's interest in petrochemicals has provided many new entrants into the chemical manufacturing business. The oil companies in most cases have established separate petrochemical subsidiaries, or separate divisions. A factor influencing this change has been the recent low growth rate of petroleum fuels which has encouraged diversification by oil companies. Petrochemicals offer the quadruple incentive of rapid growth, attractive profit potential, ability to use captive raw materials, and a technology closely related to refining. Petrochemicals are a natural step for large, integrated oil companies that have plentiful raw materials and available process equipment. In practice, petrochemical units frequently are within oil refineries and are almost indistinguishable from the adjacent oil-refining units. Petrochemicals manufacture is largely oriented toward production of raw materials. Plants generally are placed near sources of hydrocarbons from refinery streams, although low-cost transportation by tanker and pipeline has enabled some operations to be established in areas having no local sources of hydrocarbons.

LPG, which is a byproduct of oil refining and natural gas processes, is in plentiful supply and is becoming an increasingly important petrochemical raw material. Chemically LPG, preponderantly, is a mixture of propane, butane, and isobutane, with propane being about half of the total. A mature technology has been developed on production, processing, handling, and storage of LPG and its major derivatives.

A general classification by types of petrochemical product is aliphatics, aromatics, and inorganics.

Aliphatics

The production of aliphatic petrochemicals is largely based on the use of four basic materials: Ethylene, acetylene, propylene, and butylene, all of which may be derived from LPG. The installed ethylene capacity in United States in 1963 was 9 billion pounds per year, about 7 billion pounds was consumed in that year. Growth in demand is expected to continue at about 6 percent through 1970, and the largest outlet is for the manufacture of polyethylene, followed by ethylene oxide, ethyl alcohol, and styrene monomer.

Aromatics

In the aromatics field, about 80 percent of the benzene, toluene, and xylene, which are the major basic aromatic chemical building blocks, are petrochemicals produced by oil companies or their subsidiary firms. Benzene is by far the most important of the petroleum-derived aromatics, and production from petroleum is close to 600 million gallons per year. The principal uses of benzene are for manufacturing styrene monomer, synthetic phenol, and nylon. Toluene and xylenes largely are blended into motor gasoline, but there also is a substantial solvent market, and part of the toluene is converted into benzene and explosives.

Inorganics

Ammonia, carbon black, and sulfur are the major inorganic chemicals derived from petroleum and natural gas. In a typical synthetic ammonia plant, hydrogen is obtained from natural gas by steam re-forming and then combined catalytically with atmospheric nitrogen. Ammonia production reached 6.6 million tons in 1963 and was distributed to the following markets: Fertilizers, 75 percent; industrial uses, 20 percent; and exports, 5 percent. Allied major products are nitric acid, ammonium nitrate, urea, and ammonium phosphates.

Most of the carbon black produced is made in furnace black plants from aromatic oils such as side-cut or cycle stocks from catalytic cracking, although channel blacks (the traditional gas black) and gas furnace blacks also are made in substantial but diminishing amounts. High natural gas prices have resulted in a diminishing number of natural gas channel black plants in recent years. Oil black has proved to have better reinforcing properties for rubber compounding than channel black which, however, is still the preferred material in many applica-

tions. Total carbon-black production in 1963 reached 2,100 million pounds, with over 1,600 million pounds for rubber products.

Natural Gas

In 1963, natural gas consumption was 14,640 billion cubic feet, an increase of 5 percent over that of 1962. The average value at the wellhead was 15.8 cents per Mcf and 51.2 cents per Mcf at the point of consumption. Consumption of natural gas, classified according to major uses, is shown in table 2.

TABLE 2.—*Use of natural gas in the United States, in 1963*

Use:	*Quantity, million cubic feet*
Residential	3,589,021
Commercial	1,267,783
Field (drilling, pumping, etc.)	2,081,339
Carbon-black manufacture	117,378
Other industrial and utilities	7,584,959
Total consumption	14,640,480

BYPRODUCTS AND COPRODUCT RELATIONSHIPS TO OTHER ENERGY SOURCES

Byproducts

The major petroleum products, such as gasoline, kerosine, diesel fuel, and distillate fuel oil, are made to specifications designed to suit performance requirements. Some original constituents of these major products may be removed during processing to meet specifications, and these unwanted materials often have value as byproducts. Also, there often develops a use for a particular hydrocarbon or other component of the fuel so that separation of the constituent results in more advantageous use.

From the early days of the oil industry, efforts were made to separate and recover the liquids contained in the wet gas which usually accompanied crude oil production. The simple processes of compression and cooling normally accompanying the handling and movement of the gas caused some casinghead gasoline to separate. This casinghead gasoline, also called natural gasoline, could be blended into motor gasoline in small amounts but could not be used by itself as motor fuel because its high vapor pressure caused "vapor lock" in automobile engines. After most of the propane and a large part of the butane were removed from the casinghead gasoline, the vapor pressure was reduced to levels acceptable in motor gasoline. Until improved techniques were evolved for recovering these natural gas liquids and for their utilization, they often were wasted. Markets developed gradually for them, largely propane and butane, which now supply large and important domestic, commercial, and industrial fuel; and chemical markets.

Hydrogen sulfide is a common impurity which must be removed from natural gas before it is acceptable as fuel. Processes now are widely employed that not only remove this contaminant to purify the natural gas for marketing but also recover the sulfur as a profitable byproduct in the form of either elemental sulfur or sulfuric acid. Purification of natural gas by sulfur recovery and the companion steps of carbon dioxide and water vapor removal have greatly increased the supply of natural gas of a quality suitable for fuel and petrochemical uses. Capacity for producing sulfur from natural gases in the United States is approximately 1.0 million tons annually, and in 1963, 925,000 long tons of sulfur were produced. In the United States 80 percent of the sulfur consumed is used in making sulfuric acid.

Synthetic rubber is an outstanding example of a product derived from petroleum by the application of science and technology. Prior to World War II, synthetic rubber production in the United States was limited to small quantities of specialty products. Because of the shortage of natural rubber early in World War II, the Government using privately developed technology, which was just then becoming practical, supported an emergency synthetic rubber industry to meet wartime rubber demands. Butyl and butadiene-styrene copolymer rubber feedstocks were produced from fractions derived from natural gas liquids and from petroleum refinery cracking plants.

In 1960, two new synthetic rubber products, polybutadiene and polyisoprene, were developed which are outstanding rubbers, and they are rapidly capturing rubber markets. In 1950 about 41 percent of all new rubber consumed in the United States was synthetic rubber, and by 1963 its consumption had increased to 73 percent.

The helium content of some natural gases is high enough for its extraction for commercial use. This is a substantial operation of the Helium Activity, Bureau of Mines, which operates helium-extraction plants to supply the Government and industry with this unique gas. In addition to the Bureau's plants, several companies in recent years have built helium-extraction plants to remove helium from fuel gas going to market. The crude helium product is sold to the Bureau and stored in its gas reservoirs in the Texas Panhandle for future recovery and use. This is a conservation effort which now is retrieving about 3 billion cubic

feet of helium per year, most of which otherwise would be lost in fuel gas. Detailed helium information is given in the "Helium" chapter in the bulletin.

Examples of product and byproduct development are extensive and the list continues to grow. The trend will continue because of the virtually endless potential of petroleum, the basic fuel and chemical raw material.

Relationships to Other Energy Sources

Petroleum and its products compete with other fuels for some uses and have a virtual monopoly in other fields. Gasoline has no successful competitor as a passenger-car fuel, although other methods of applying motive power, such as steam and electricity, were utilized, but discarded, over a quarter century ago. For some commercial vehicles and trucks there is competition between the three petroleum fuels: gasoline, diesel oil, and LP gases. Diesel locomotives have performed so well for American railroads that the majority of them now have converted to diesels. In aviation, gasoline remains important, but kerosine and jet fuels are gaining as the use of jet engines increases and use of piston engines declines. No fuels other than gasoline, kerosine, and jet fuel are being used in aircraft or are being contemplated as present.

Relationships to Other Fuels

In commercial and industrial heating and in the generation of steam and power, both petroleum and natural gas fuels are on a more equal basis with other fuels. In these applications, price frequently is more decisive than it is in domestic or small commercial uses where convenience and related factors outweigh the price advantages of other fuels. Petroleum and solid fuels are both undergoing experimental trials in gas-turbine-powered railroad locomotives The choice of fuel ultimately will be determined by performance and overall operating costs. Another approach in fuel-energy conversion studies is that of the fuel cell. The energy principal involved in the fuel cell is the conversion of fuel to electricity without such intermediate steps as burning to produce steam, or operating an internal combustion engine to drive an electrical generator.

The oil industry is working currently toward what is termed a total energy concept which is an effort to retain, or even to regain, that part of the market that has been converting from oil to the use of natural gas and electricity for heat. The total energy concept involves on-site generation of electricity in a commercial or industrial facility using a gas turbine or an internal combustion engine, as a prime mover to drive an electric generator. Heat, normally wasted, is recovered from the exhaust of the prime mover, and in the case of engines, from jacket cooling water, and diverted to useful work. The concept is applicable to commercial establishments, office building, schools, hospitals, motels, and apartment complexes. It is particularly attractive to industrial applications in remote areas and in situations requiring large volumes of process heat and steam. In all applications a prime consideration in this concept is the cost of fuel. Fuel selection is decisively governed by the economics of available fuel sources and in some locations economics favors natural gas over oil.

Other fossil fuels are receiving attention in the fuel-energy source picture. Among those receiving attention are oil shale, tar sands, and gilsonite. Gilsonite is used on a small scale and the huge oil shale resources of the West are under study as a source of liquid fuels to supplement petroleum. No active work is underway in the United States on tar sands, but active commercial operations have been undertaken in Canada. Currently, the Bureau of Mines Oil Shale Research Center near Rifle, Colo., has been reactivated by lease to industry. The facility is leased to the Colorado School of Mines Research Foundation which is operating it experimentally for six oil companies to investigate on a pilot-plant scale, economic methods of extracting oil from shale (for additional information, refer to "Oil Shale" chapter).

RESERVES

Attempts to estimate the magnitude of oil and gas reserves in the early years of the petroleum industry appear to have been prompted primarily by scientific curiosity. Most of the early appraisals were made by comparing declining productivity with that of fields which already had neared depletion. Later, reserve estimates were required for business and tax purposes, such as the Revenue Act of 1918 which required oil and gas producers to determine their recoverable reserves for oil and gas on owned or leased acreage. In fact, because of the income tax law, one of the early comprehensive publications on oil reserves was published in 1919 by the U.S. Treasury Department assisted by the Bureau of Mines and Geological Survey. Many of the concepts now in use, especially on decline in natural-gas production, were presented in this report. In 1936, the American Petroleum Institute created a Committee on Petroleum Reserves. Subsequently, each year this committee has computed the reserves of crude oil

in the United States which are recoverable under existing economic and operating conditions. In 1945, and annually thereafter, the Committee on Natural Gas Reserves of the American Gas Association has published its authoritative study of proved natural gas reserves.

Proved reserve figures are no more than a working inventory of oil and gas already discovered and recoverable under existing conditions. This inventory does not represent the total amount of oil or gas in existence at any given time, but merely the amount of oil and gas the industry has already proved by drilling. Under this system of estimating petroleum reserves, large amounts of oil are not reported which undoubtedly will be produced later after improved production techniques are applied. These incremental amounts in most cases are not included in proved reserve statistics until their recovery is virtually a demonstrated certainty. Hence, reserve estimates are subject to future revision, although the established proved reserves estimates are as accurate as possible on their issue date.

The quantity of liquid or gaseous hydrocarbons in a reservoir that can be classed as proved reserve involves knowledge of the physical characteristics of the reservoir rock and the oil or gas contained therein.

Some of the factors required for estimating reserves are: areal extent of the productive reservoir, production history, geologic structural features of the reservoir, and the characteristics of the reservoir rocks and fluids. Included in these characteristics are chemical and physical properties, porosity, permeability, and amount of oil and water in the pore spaces of the rock. Other important determinations are the type of driving mechanism that provides the natural reservoir energy, such as fluid expansion, free (external) gas cap, solution (internal) gas and water or gravity drive.

Many basic data used in preparing reserve estimates are obtained by the industry while carrying our normal exploratory and development programs. To operate and maintain a successful position in this highly competitive business, oil companies assemble data on the availability of their reserves. The aggregate of these individual company estimates obtained from the technical staffs of the companies, and published by trade organizations and technical journals, provides the most comprehensive overall estimates that are now available as published information. Much petroleum research is carried on in the industry and by private industrial laboratories and universities to develop additional information and data.

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World

The international petroleum industry is growing vigorously. At the end of 1963, worldwide crude oil reserves were estimated at 326 billion barrels as shown in figure 1, table 3 (*9*). This is a record volume which has increased 20 percent since 1958. It reflects in part the present strong interest and development of offshore areas which only a few years ago were considered remote possibilities. Worldwide importance of offshore oil is increasing because of the vast reserve potential of good reservoir structures on the continental shelves in comparison with the comparatively fewer favorable prospects on shore. Many petroleum firms are more willing to risk capital in offshore ventures and pay the higher development costs because of better success ratios there, which in some cases are aided by lower sea transportation costs to markets. Recent progress in resolving the legal problems associated with offshore concessions has provided a strong inducement to offshore exploration. This is especially true in offshore areas in the United States and Europe, in the North Sea areas adjacent to Germany, the Netherlands, and the United Kingdom.

TABLE 3.—*Estimated world proved reserves of crude petroleum in 1963*

[Million barrels of 42 U.S. gallons]

Area	Dec. 31, 1958	Dec. 31, 1963	Percent increase	Ratio of reserves to 1963 production
North and Central America	36,736	38,455	4.7	12.3–[1] 11.3
South America and Caribbean	19,643	22,885	16.5	15.8–8.7
Western Europe	1,402	1,686	20.3	14.5
Eastern Europe (including U.S.S.R.)	27,170	33,441	23.1	20.9
Middle East	173,951	204,821	17.7	82.4
Africa	4,119	15,015	264.5	[2] 35.8–[3] 23.4
South Asia, Far East, and Oceania	10,146	10,322	1.7	[4] 24.0–[5] 46.7
World total	273,167	326,625	19.6	34.5

[1] United States.
[2] Northern Africa.
[3] Western Africa.
[4] Asia, Far East.
[5] Oceania.

Source: World Oil.

Venezuela's recent reserve additions are in offshore areas in Lake Maracaibo. In the Middle East, where five-eighths of the known oil reserve of the world has been found, important proved reserves recently have been added, especially in the Persian Gulf area. The Middle East now has an 82.4 to 1 reserve to production ration. Shown in table 3 are these ratios and proved reserves for other areas of the world.

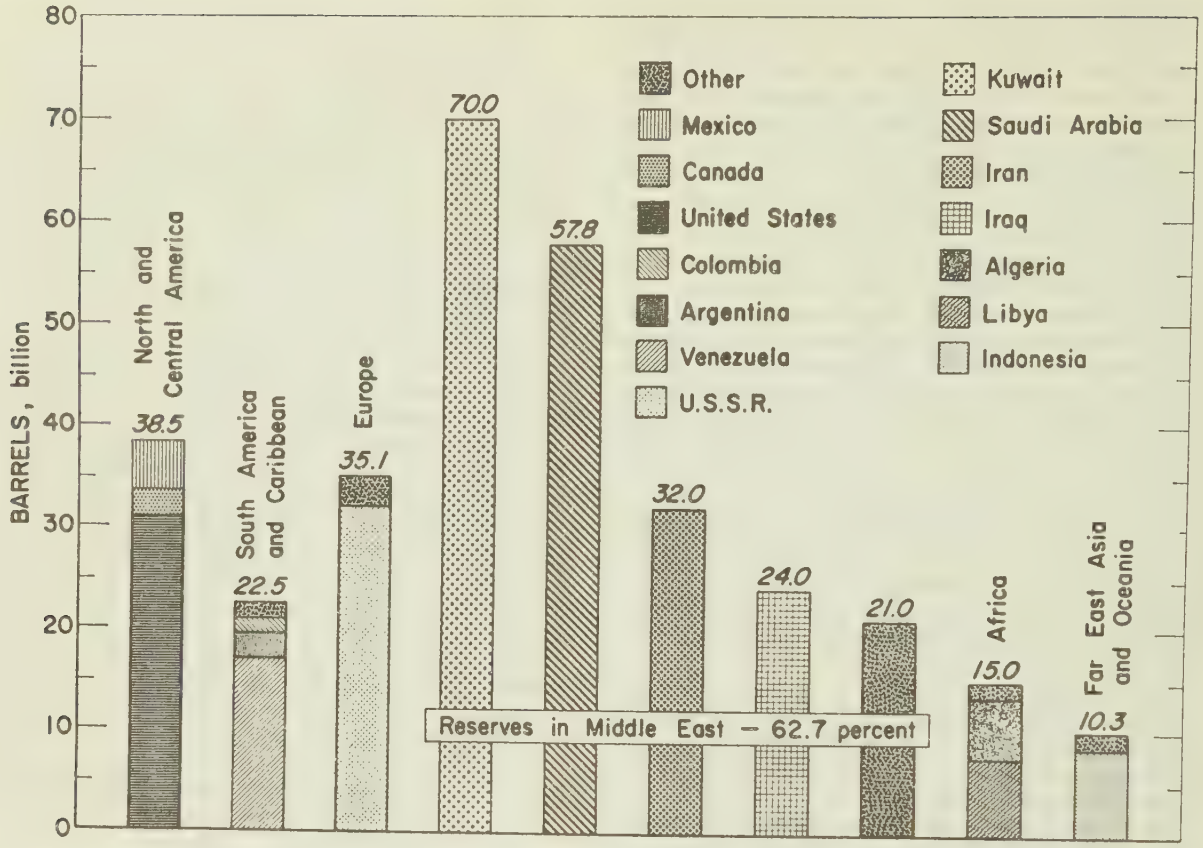

FIGURE 1.—Estimated 1963 Proved Crude Oil Reserves in the World.

United States

Exploration and the consequent discovery of new oil reserves by the industry is interrelated with supply and demand for crude oil and its products at prices that will compensate for the cost of exploration. For example, the flood of oil that became available after the discovery of the East Texas field in 1930 and the decrease in both demand and crude oil prices during the depression years of the early 1930's were reflected by fewer discoveries of new reserves for several years in the early and midthirties. Similarly, the flush production from the large reserves discovered in the Illinois basin in 1937 and in subsequent years affected the annual rate of discovery for several years.

During World War II the shortage of manpower, machinery, and low priorities for exploration resulted in a lower-than-normal amount of reserves discovered during that period. Within the past decade a large excess of petroleum-producing capacity has been built up in the United States, and allowable rates of production per well have been curtailed. Some results of this are a lessened initiative to explore and a decline in both the annual number of exploratory wells drilled and number of discoveries.

The estimated proved reserves of liquid hydrocarbons by States, prepared by American Petroleum Institute and the American Gas Association as of December 31, 1963, are shown in table 4. The total reserve of 38.6 billion barrels consists of 30.9 billion barrels of crude petroleum and 7.7 billion barrels of natural-gas liquids (*2*).

The estimated proved reserves of natural gas in the United States, prepared by the American Gas Association as of December 31, 1963, amount of 276.2 trillion cubic feet; which data are summarized in table 5 (*1*).

CONSERVATION

Petroleum conservation by common usage and statutory definition is prevention of reasonably avoidable waste of oil or gas aboveground and underground in drilling, production, and storage operations. Conservation is brought about by technology in the finding, development, production, and utilization of oil and gas. Such is

the use of sound engineering practice which combines in application both economic and scientific principles.

TABLE 4.—*Estimated proved reserves of liquid hydrocarbons, December 31, 1963*

[Thousand 42-gallon barrels]

State	Crude oil	Natural gas liquids	Liquid hydrocarbons
Alabama	45,069		45,069
Arkansas	225,291	18,695	243,986
California [1]	3,599,735	290,070	3,889,805
Colorado	368,375	21,990	390,365
Illinois	416,612	3,744	420,356
Indiana	63,432	95	63,527
Kansas	841,349	169,241	1,010,590
Kentucky	100,456	51,005	151,461
Louisiana [1]	5,088,605	1,840,823	6,929,428
Michigan	68,543	5,326	73,869
Mississippi	384,909	33,148	418,057
Montana	271,253	9,978	281,231
Nebraska	83,583	2,775	86,358
New Mexico	1,010,729	558,233	1,568,962
New York	18,435		18,435
North Dakota	389,158	82,017	471,175
Ohio	87,814		87,814
Oklahoma	1,628,138	328,193	1,956,331
Pennsylvania	91,734	1,437	93,171
Texas [1]	14,573,125	4,042,358	18,615,483
Utah	219,576	46,591	266,167
West Virginia	57,303	68,779	126,082
Wyoming	1,254,306	99,480	1,353,786
Miscellaneous	82,460		[2] 82,460
Total	30,969,990	7,673,978	38,643,968

[1] Includes offshore reserves.
[2] Includes Alaska, Arizona, Florida, Missouri, Nevada, South Dakota, Tennessee, and Virginia crude and Alabama and Florida natural gas liquids.

Source: American Gas Association and American Petroleum Institute.

TABLE 5.—*Estimated proved reserves of natural gas in the United States, Dec. 31, 1963*

[Million cubic feet—14.73 psia, at 60° F]

State:	*Reserves*
Alaska	1,690,724
Arkansas	1,792,644
California [1]	8,865,726
Colorado	1,876,057
Illinois	168,595
Indiana	60,180
Kansas	17,994,235
Kentucky	1,085,236
Louisiana [1]	75,364,992
Michigan	722,812
Mississippi	2,481,627
Montana	598,131
Nebraska	100,042
New Mexico	15,037,822
New York	132,285
North Dakota	1,119,575
Ohio	748,187
Oklahoma	19,138,820
Pennsylvania	1,214,498
Texas [1]	117,809,376
Utah	1,638,324
Virginia	31,303
West Virginia	2,311,164
Wyoming	3,988,546
Other states [2]	180,332
Total	276,151,233

[1] Includes offshore reserves.
[2] Includes Alabama, Arizona, Florida, Iowa, Maryland, and Missouri.

Source: American Gas Association.

The petroleum industry has been the leader in supplying the Nation's expanding economy demands for fuel energy in the past several decades. The rapid industrial and agricultural output of the United States and continued improvement of living standards have been aided to a substantial extent by an abundant supply of low-cost fuels for heat, light, power and transportation.

Oil and gas have been a primary source of such low-cost fuels and presently supply approximately three-fourths of the total U.S. fuel energy requirements. In addition, oil and gas are raw materials for a vast number of essential products that are of common daily use. Continued progress in technology, operating practices, and conservation practices will be imperative if anticipated requirements are to be met.

Conservation implies more than simply saving resources to meet possible future needs or hoarding. All minerals are wasting (in the sense of diminishing) resources and, therefore, are irreplaceable. Oil and natural gas are not known to be replaced by natural geologic processes at a rate sufficient to maintain a commercial supply.

In 1963, U.S. oil production amounted to 2.8 billion barrels. This output was made possible mainly through the continuous, orderly development and expansion of the industry. A major factor in the present output and productive capacity has been the growing use of conservation practices that each year result in the recovery of larger shares of the oil in place than was obtained formerly.

The future supply of petroleum is determined both by past discoveries and current and future discoveries. Reserves at any time fix merely the possible portion withdrawable at that time. Continuity of supply is dependent on exploration and development drilling, both of which are financed by the industry's current profits and venture capital. Therefore, the future petroleum supply is dependent upon the industrial and financial health and vigor of the oil industry.

Many of the problems of oil and gas conservation arise from the nature of petroleum, the conditions under which it exists underground, and the methods by which it is recovered. Proper consideration and understanding of these factors require detailed knowledge of the physical characteristics of the reservoir and the effect on recovery and ownership rights of various development and production methods that may be utilized. Engineering research studies and operating experience have proved that reservoirs may be produced to the point of depletion efficiently with a small number of properly located wells. The size of a plot of land for a drilling unit assigned to a well should be

the maximum area that can be drained efficiently and economically. Inadequate natural energy forces should be supplemented as early as economically justified by injection of fluids to achieve greater ultimate recovery.

Since 1910 the Bureau has pioneered in oil and gas research and studies of the Nation's petroleum resources to provide a sound technologic basis for oil and gas conservation through prevention of waste, greater recovery, and efficient utilization. The Federal Geological Survey has conducted programs relating to reserves, mapping, and geology. Both Federal agencies in cooperation with industry and State regulatory groups have recommended and supported oil and gas conservation.

The laws and regulations of the various States should encourage utilization of improved technology, such as the methods stated to assure maximum economic recovery of oil and gas. Revisions of statutes and regulations are needed as time passes to accompany improvements in technology.

Federal laws authorizing the Interstate Oil Compact Commission and the Connally Hot Oil Act have supplemented State conservation efforts and have aided enforcement of State laws.

SOURCES OF STATISTICAL INFORMATION

The principal source of petroleum and natural gas information presented herein is the Bureau of Mines, Minerals Yearbook, volume II, and Bureau of Mines, Mineral Industry Surveys. Other Government sources are the Federal Power Commission, Bureau of the Census, Maritime Administration, Bureau of Labor Statistics, Bureau of Public Roads, and Business and Defense Services Administration. Oil industry organizations providing statistical data include: American Petroleum Institute, American Gas Association, Independent Petroleum Association of America, American Association of Petroleum Geologists, Interstate Oil Compact Commission, American Association of Oil Well Drilling Contractors, and the National Petroleum Council.

Secondary sources include State agencies, petroleum and natural gas periodicals, technical journals, trade publications, individual companies, as well as numerous publications of foreign governments.

PRODUCTION, CONSUMPTION, AND TRADE

In 1963 world crude-oil production was 9.5 billion barrels, of which the United States produced 29 percent, or 2.8 billion barrels, as shown in table 6.

The demand for natural gas has increased about 6 percent per year for the last decade. Marketed production of natural gas reached 14.7 trillion cubic feet in 1963, as shown in table 7.

World consumption of petroleum continued to increase in 1963. The U.S. increase was about 6 percent and the rest of the free world the increase was about 10 percent.

TABLE 6.—*Salient statistics of crude petroleum, refined products, and natural gas liquids in the United States*

	1959	1960	1961	1962	1963
Crude petroleum:					
Domestic production—thousand 42-gallon barrels	2,574,590	2,574,933	2,621,758	2,676,189	2,752,723
World production—do	7,144,860	7,689,851	8,183,863	8,882,218	9,535,434
U.S. proportion—percent	36	33	32	30	29
Imports [1]—thousand 42-gallon barrels	352,344	371,575	381,548	411,039	412,660
Exports [2]—do	2,526	3,087	3,227	1,790	1,698
Runs to stills—do	2,917,661	2,952,534	2,987,158	3,069,631	3,170,652
Value of domestic production at wells:					
Total—thousand dollars	7,473,336	7,420,181	7,565,582	7,774,051	7,965,743
Average per barrel	$2.90	$2.88	$2.89	$2.90	$2.89
Refined products:					
Imports [3]—thousand 42-gallon barrels	297,239	292,536	318,118	348,754	362,053
Exports [4]—do	74,541	70,819	60,336	59,600	74,216
Output of gasoline [5]—do	1,488,860	1,522,497	1,534,462	1,583,376	1,625,198
Yield of gasoline—percent	44.9	45.1	44.7	44.8	44.1
Average dealers' net price (excluding tax) of gasoline in 55 U.S. cities—cents per gallon [6]	16.09	16.08	15.80	15.45	15.22
Natural gas liquids:					
Production—thousand 42-gallon barrels	320,757	340,157	361,689	372,705	400,886
Stocks, end of year—do	24,887	28,931	37,067	31,385	33,747

[1] Bureau of Mines data for crude oil and unfinished oils.
[2] U.S. Department of Commerce data, except those for Hawaii (before 1960) which are Bureau of Mines data. Exports include shipments to territories.
[3] U.S. Department of Commerce data, except for unfinished oils.
[4] New basis. These data are comparable to 1963 due to product reclassification resulting from separately reporting data for petrochemical feedstocks.
[5] Beginning with 1961 excludes unfinished gasoline.
[6] Platt's Oil Price Handbook.

TABLE 7.—*Salient statistics of natural gas in the United States*

	1959	1960	1961	1962	1963
Supply:					
Marketed production [1] million cubic feet	12,046,115	12,771,038	13,254,025	13,876,622	14,746,663
Withdrawn from storage do	668,743	712,658	698,050	854,336	916,720
Imports do	133,990	155,646	218,860	401,534	406,204
Total do	12,848,848	12,639,342	14,170,935	15,132,492	16,069,587
Disposition:					
Consumption do	11,819,638	12,509,427	13,081,714	13,890,129	14,640,480
Exports do	18,413	11,332	10,747	15,814	16,957
Stored do	787,485	844,352	843,666	940,823	1,047,492
Lost in transmission, etc do	223,312	274,231	234,808	285,726	364,658
Total do	12,848,848	13,639,342	14,170,935	15,132,492	16,069,587
Value at wellhead:					
Total thousand dollars	1,556,800	1,789,970	1,996,241	2,145,301	2,328,030
Average cents per Mcf	12.9	14.0	15.1	15.5	15.8

[1] Comprises gas sold or consumed by producers, including losses in transmission, amounts added to storage, and increases in gas in pipelines.

Imports of all oils in 1963 increased 17.8 million barrels to a total of 777.6 million barrels. Residual fuel oil imports accounted for 56 percent of the increase and military jet fuel, 30 percent. The additional imports of residual fuel oil were needed to meet the demand requirements of east coast consumers, because of the decline in the supply available from domestic sources.

Exceptionally cold weather during the first part of 1963 in Europe which required large shipments of fuel oils to relieve the fuel shortage there was responsible for reversing the downward trend in exports for the past several years. In 1963 exports of petroleum increased from 61.4 million barrels in 1962 to 75.9 million barrels.

Under the Tariff Schedules of the United States, effective August 31, 1963, imports of crude petroleum are dutiable at the rate of 5¼ cents per barrel if under 25° API, or at 10½ cents per barrel if above 25° API. Rates on petroleum products are 1¼ cents per gallon for gasoline and other motor fuel (including diesel oil intended for use in diesel engines), 2 cents per gallon for lubricating oil, ¼ cent per gallon for other liquid derivatives of petroleum (including liquid petroleum asphalt) except medicinal-grade mineral oil, and ½ cent per pound of paraffin wax and other petroleum wax products. These rates apply only to imports from non-Communist countries; rates for Communist countries are somewhat higher.

GOVERNMENT PROGRAMS

Responsibility for petroleum and natural gas conservation rests chiefly with the States through powers derived from the Constitution, although the Federal Government exerts influence, both direct and indirect, on State conservation programs.

Conservation of petroleum (and other resources as well) is practiced by the Federal Government by regulation of those who operate on lands of the public domain and on those submerged lands of the Continental Shelf which are owned by it; the Government serves also as steward of Indian lands. In these capacities the Federal control and sponsorship of conservation is important to a substantial part of the Nation's petroleum reserves.

In both World War II and the Korean war, the Government encouraged and provided financial incentive to industry for enlarging producing and refining capacities in excess of peacetime requirements. Some of this excess remains, and it has sharpened the need to practice conservation. Rigid production control by the States and by the industry has maintained a capacity adequate for peacetime needs and provided sufficient additional capacity to meet emergencies, as was demonstrated during the Suez crisis.

In furtherance of policy set forth by the Congress to meet the "urgent need" for offshore exploration and development, the Government has offered lands for oil and gas leasing whenever the industry has indicated it is ready to bid for leases. This policy has resulted in widely spaced big lease sales rather than uniformly spaced small sales. Caution has been exercised to discourage a disproportionate commitment of industry capital to offshore exploration and development at the expense of onshore areas. Outer Continental Shelf leases have been sold with a minimum bonus requirement of $15 per acre, with rentals or minimum royalty at $3 per acre per year.

The Federal Government has always included conservation requirements in lease terms and conditions and has cooperated with the States in application and enforcement of spacing and production restrictions. Since 1930 the Government has been a foremost proponent of the development of the Nation's oil and gas resources under unit plans of operation.

Petroleum conservation programs of the States are supported indirectly by the Federal Government. These programs are aided by the Bureau of Mines' Monthly Petroleum Forecast and the Forecast of Market Demand for Crude Oil.

The Bureau does not allocate crude production quotas to any State or area. Information derived principally from the industry is analyzed and used to determine the month-to-month need for crude oil and products. This, and similar information from many other sources, is used by the States in their production-proration programs. The Bureau's forecast of demand does not consider price. The consensus is that demand for petroleum and its products is inelastic for short periods so that the effects of monthly price variations on the demand forecasts are negligible.

The Interstate Oil Compact Commission was authorized by law in 1935. It serves as a forum for interstate problems, and indirectly and to a lesser degree for intrastate problems. The activities of the Compact have a direct strong influence on petroleum conservation. Through this Commission's activities, State laws and policies in matters of oil and gas production tend more toward uniformity and are coordinated to the benefit of the entire Nation.

The Federal Government, in recent years, has used its authority under the 1958 extension of the Trade Agreements Act which provides for limiting commodity imports that threaten the economy and national security. Currently, the Department of the Interior establishes oil-import quotas under this act that have an influence on U.S. oil production. Licenses are issued to authorized importers which permit them to import crude oil or petroleum products into specified refinery districts in which the importers qualify. All licensors are required to process the crude oil they import in their own refineries, unless they exchange their foreign oil for domestic oil. In that event, they must process this domestic oil in their plants. Authorized importers are not allowed to sell, transfer, or reassign their allocations or licenses to any other person.

The Federal Power Commission under the authority of the Natural Gas Act of 1938 (and as amended) regulates interstate commerce in natural gas.

The Department of Justice and the Federal judiciary also affect conservation of petroleum and natural gas. In circumstances where operations are practiced to control markets and prices, the Department of Justice takes restrictive legal action. The Justice Department reports annually concerning the Interstate Oil Compact Commission. These reports cover the entire spectrum of the oil industry and are not confined merely to conservation and Compact matters.

Petroleum is unquestionably a necessity to both peacetime and wartime economies. In war, suddenly expanded military requirements are added to necessary civilian requirements that must be satisfied at a level to insure an efficient homefront. In both World War II and the Korean war, it proved practical to have Government petroleum matters centralized as much as possible in one agency. During World War II, this agency was the Petroleum Administration for War (PAW) and during the Korean war, the agency was the Petroleum Administration for Defense (PAD). These agencies were responsible for determining the amount and location of available supplies of petroleum and how they could best be used to meet the needs of the United States and its allies.

Petroleum is found in many countries with which the United States has collective security-treaty relationships. Hence, the national security of the Nation is closely alined with that of its treaty allies. An expanding domestic oil industry, plus a healthy oil industry in friendly countries, constitute important elements in an industrial strength which contributes to strong national defense. In this, both domestic production and imports are essential.

Oil has a vital role in national security and is one of the major essential items in military needs. Petroleum cannot be economically stockpiled; the quantities required are too great. An oil stockpile actually is measured in refining capabilities, pipeline throughput, capacities of storage terminals, and producibility and deliverability of proved reserves of crude oil in the ground.

The continuing mechanization of military equipment and greater mobility of troops portend a steady increase in petroleum requirements. It appears that with few exceptions military equipment will continue to derive energy from liquid petroleum and its products. Some naval ships now have nuclear power, but it is not likely that there will soon be any appreciable decrease in the Navy's petroleum-fuel requirements.

PRICES AND COSTS

The costs of finding and bringing a particular oil or gas field into production have no direct relation to the value that will be received for the output of that field. The costs of finding petroleum (exploratory costs) depend upon the following factors: (1) Area that must be surveyed before a favorable structure is found; (2) complexity of the geologic formations studied in deciding on a favorable location; (3) accessibility of the selected site to men and equipment; and (4) terms agreed upon with the landowner for his mineral rights. Drilling costs will vary with the geographical location of the well, the type of formations penetrated, the depth of the producing formation, and the character of the oil-producing formation. There is no certainty that oil in producible quantities will be found by the first well drilled or by any well drilled—in which case the total expenditure is a loss. And moreover, if oil or gas is found, the financial success of the venture still depends on the extent and quality of the reserves as well as the price obtained for the output.

Data on costs and trends of drilling and completing oil and gas wells are of interest to many in business and industry as well as officials in Government who formulate and administer national energy resource policies (*8*). Cost data is held in confidence by most oil and gas companies. A widely quoted source of such data is the Joint Association Survey. This study is undertaken by the Cost Study Committee of the Independent Petroleum Association of America in cooperation with the American Petroleum Institute, and the Mid-Continent Oil & Gas Association. A survey was published in 1964; previous surveys were conducted and published in 1953, 1955–56, 1959, and 1962. These surveys present statistical information of the cost of drilling and equipping wells and expenditures incurred by oil and gas operators during a year incident to the finding, developing, and producing of oil and gas.

In 1954, the Supreme Court decreed that the Federal Power Commission should regulate the price of gas sold by producers in interstate commerce. As a result of this decision, the FPC obtained and published many records and statistics in its effort to develop a cost-of-service approach to the regulation of gas prices.

A lack of reliable data has made it difficult to appraise the economic factors and costs in the exploration and production of oil. The cost categories most used are as follows: (1) finding or exploration, (2) development, and (3) production or lifting. Finding or exploratory costs include: leasing; geological and geophysical operations; drilling of exploratory wells, which includes completing successful wells; and installing wellhead connections.

Development costs encompass all items necessary to develop an oil pool following discovery. These include outlays to equip the discovery wells beyond the wellhead for production; for drilling additional wells to define pool limits; and later, expenditures for pressure maintenance and secondary recovery.

Production cost is a straightforward accounting of costs for pumping or lifting, field maintenance, other operating expenses, and continuing expenditures on land use operations.

The potential profits of oil producing are indicated by analyses of replacement costs which are the sum of finding, developing, and operating, usually expressed on a per-barrel basis. This apparently simple relationship actually is difficult to compute because finding costs incurred at present must be related to costs and returns obtainable at some future time when oil is produced, and this production may be spaced over many years. Current development costs likewise must be referred to those pertaining to some future quantity of oil that will have been made recoverable, overtime, by the outlays. When a calculation is made of finding costs for a given year in relation to development costs, the reference may not be exact because such costs may or may not have been incurred in the same year or spaced closely enough in time to be economically or technologically comparable.

The general trend in oil prices over the past 5 years is shown in the Independent Petroleum Association of America's price index. The crude-petroleum index is the weighted-average well price for eight principal areas and closely approximates the average price of all crude oil in the United States. The refined-products index also is a weighted-average refinery price of gasoline, kerosine, and light and heavy fuel oils for nine principal areas, calculated from low quotations reported weekly by the National Petroleum News. From 1958 to 1963 the crude-petroleum index ranged from $3.12 to $2.98 per barrel and the refined products index, from $3.89 to $3.79 per barrel. At present the value added by refining is 77 to 81 cents per barrel, or less than 2 cents per gallon. The index shows the narrow margin and the competitive nature of the petroleum industry.

The Joint Association Survey of drilling costs in the United States for 1962 shows that the total petroleum industry expenditures for drilling and equipping wells amounted to $2.6 billion, or an increase of 7.5 percent over 1961 (*5*).

The costs reported in the survey include both tangible and intangible costs for drilling and

completing wells up to and including the "Christmas Tree," but exclude surface equipment such as pumping units, and tanks, as well as exploration, development, and production costs which will be reported in part 2 of the survey at a later date.

In 1962, the average productive well was 4,326 feet deep and cost $63,435 (see fig. 2 and table 8). These represent an increase in depth of 2.6 percent and an increase of 5 percent in costs over that of the preceding year.

The trends of averages in depths and cost per foot of productive wells and dry holes for 1955–62 are shown in table 8 and figure 2. Average depth of productive wells increased 315 feet from 4,011 to 4,326 feet, and the average cost per foot rose by $1.72 per foot from $12.94 to $14.66 from 1955–62.

Since 1955, the average depth of dry holes has risen from 4,051 to 4,533 feet, costs per well have increased from $37,300 to $50,800, and the average cost per foot of dry hole has risen from $9.21 to $11.20.

A comparison of the averages of depth per well and cost per foot of gas and oil wells in 1962 is shown in figure 3, table 9, indicating a higher cost and a greater depth for gas wells. On an average, gas wells are more expensive to drill and complete than oil wells because of greater depth and completion charges. These higher completion charges result because the average gas well has a thicker producing formation and requires more perforations, cementing, fracturing, logging, and related services than the average oil well.

Some 700 wells were drilled offshore in 1963. Approximately 90 to 95 percent of these wells were in Louisiana offshore, and the remainder were drilled offshore from California, Texas, and Florida.

The average offshore gas well completed in 1962 cost 42.5 percent more than an offshore oil well ($495,792 versus $348,011) (*5*). Offshore gas well depth averaged 10,961 feet in 1963, 1,236 feet deeper than in 1962.

Average refining operating costs during 1958–63 have been relatively stabilized and actually slightly reduced from $1.26 per barrel of crude in 1958 to $1.23 per barrel, crude in 1963 (*7*).

Chemicals, catalysts, and gasoline anti-knock-improver costs decreased from $0.21 per barrel of crude in 1958 to $0.19 per barrel of crude in 1963, primarily through more efficient catalyst utilization. These savings were offset to a major extent by increases in costs of purchased fuel and power, insurance, taxes, royalties, and research.

TABLE 8.—*Average per well depths and costs, oil and gas*

	1955	1956	1959	1960	1961	1962
Productive wells:						
Average depth—feet	4, 011	4, 071	4, 088	4, 259	4, 218	4, 326
Average cost per well	$51, 900	$55, 600	$60, 100	$62, 200	$60, 400	$63, 435
Average cost per foot	$12. 94	$13. 64	$14. 70	$14. 60	$14. 33	$14. 66
Dry holes:						
Average depth—feet	4, 051	4, 054	4, 240	4, 168	4, 284	4, 533
Average cost per well	$37, 300	$41, 600	$43, 000	$44, 000	$45, 200	$50, 800
Average cost per foot	$9. 21	$10. 26	$10. 13	$10. 56	$10. 56	$11. 20

Source: Independent Petroleum Association of America.

TABLE 9.—*Summary of U.S. drilling in 1962*

	Oil	Gas	Dry	Total
Wells drilled	21, 402	5, 858	16, 684	43, 944
Footage drilled (thousands)	86, 494	31, 432	75, 631	193, 557
Expenditures (millions)	$1, 161	$569	$847	$2, 577
Average depth per well—feet	4, 041	5, 366	4, 533	4, 405
Average cost per well	$54, 223	$97, 093	$50, 793	$58, 635
Average cost per foot	$13. 41	$18. 10	$11. 20	$13. 31

Source: Independent Petroleum Association of America.

TAXES

The taxes paid by or through the petroleum industry are multiple and varied. In addition to the income and property taxes to which all companies are subject, most oil-producing States impose a tax on each barrel of crude withdrawn from the ground, many States collect inspection fees on petroleum products, and finally, there are Federal, State, and some city taxes on gasoline, on diesel fuel used in highway transportation, and on lubricating oil. It is reported from a Chase Manhattan Bank study of 33 selected oil companies that in 1962 they paid $2.3 billion as indirect taxes to domestic and foreign governments, 9 percent above the amount of 1961. These companies collected $5.5 billion from the public in excise and sales taxes and paid a total to governments of $7.8 billion, which was more than double the companies net earnings that year. During 1959–61 the oil industry paid 4.9 percent of its gross income as direct taxes, com-

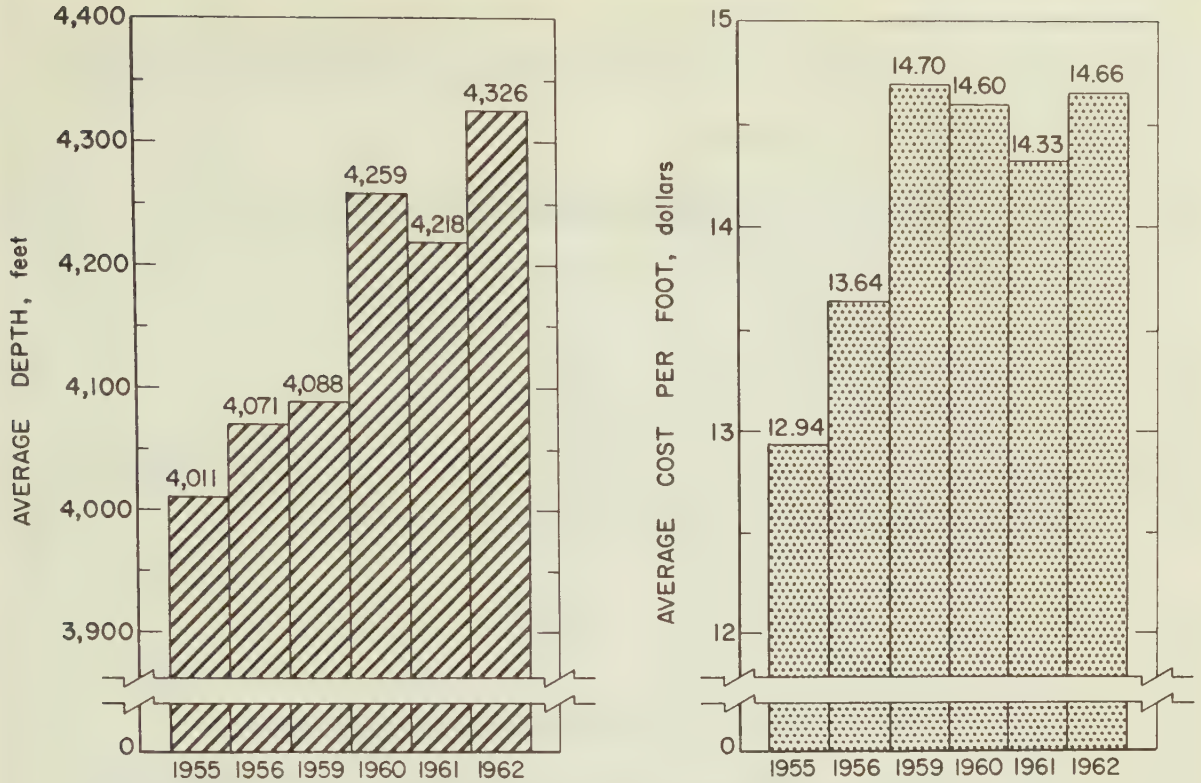

FIGURE 2.—Average Depth per Well and Costs per Foot of Productive (Oil and Gas) Wells in the United States.

pared with 5.1 percent for all manufacturing and mining, and 4.5 percent for all business. The Chase Manhattan study shows that a typical oil well in the United States generates direct tax payments to local State and Federal Governments of about 63 cents per barrel of crude oil. The indirect taxes on the products from a single barrel of crude are about $1.60.

Three tax provisions contained in the Federal income tax law are pecularily relevant to the oil industry. These are the intangible writeoff, depletion allowance, and foreign tax credit. Intangible writeoff provisions permit the option to deduct as expense, intangible drilling and development costs, or to capitalize such costs and recover them through the depreciation deduction. Intangible expenses have not been clearly defined, but they are generally understood within the industry to be expenditures for items not having salvage value. Many expenses are indeterminate within the provision, particularly in offshore operations where many of the expenses incurred are controversial. The intangible writeoff is available for all operations, whether a small independent operator or large integrated oil company. The deduction serves a useful purpose to the oil industry by permitting early recovery of capital to be available for other purposes.

Producers of oil and gas are allowed to deduct an allowance for depletion. The principle of depletion allowance in its present form, as far as the oil industry is concerned, began in 1926. Depletion may be calculated in the oil industry upon one of two bases. One formula provides for cost depletion which assures tax-free return of the original capital investment in property by amortizing part of that cost each year in proportion to the year's production, relative to the estimated total production ultimately recoverable. Producers may take as a deduction for each property the lesser of: (1) 27.5 percent of its gross income; or (2) 50 percent of the net income from the property computed without any allowance for depletion.

Transportation and Storage

Pipelines and tankers provide the primary transportation for petroleum, although tank trucks play an important part in short-haul transportation, and railroad tank cars for transportation of specialty products.

In 1963, pipelines delivered 75 percent of the crude oil to U.S. refineries, tankers and

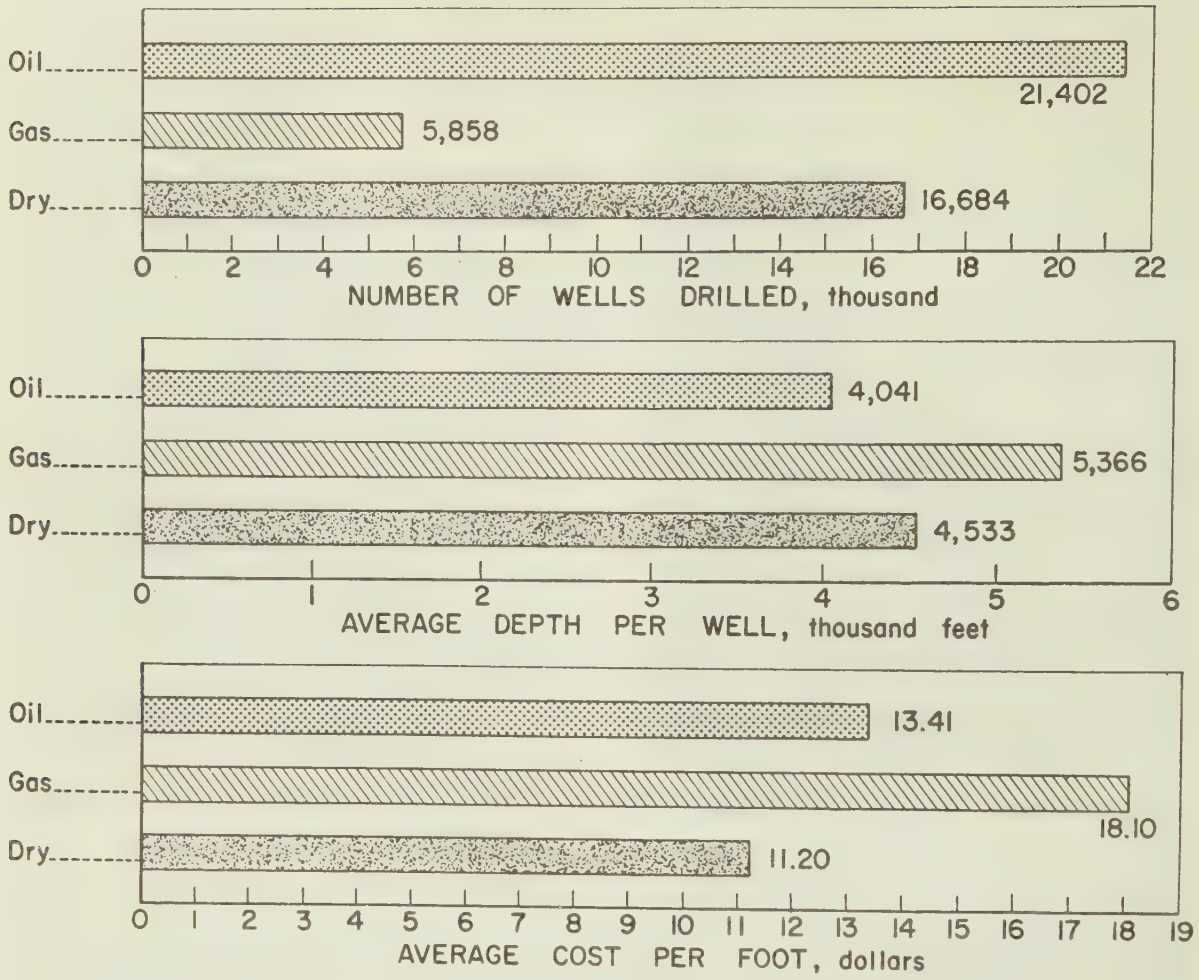

FIGURE 3.—Summary of Drilling in the United States in 1962.

barges 24 percent, and railroads and trucks about 1 percent. Of the crude oil delivered to refineries by tanker, the sources were 58 percent domestic and 42 percent foreign. Pipelines moved 45 percent of the bulk refinery products; tankers 25 percent; and barges, railroads, and tank trucks the remainder. Final delivery of nearly all finished petroleum products was made by truck, but delivery to large users, such as air terminals, is being made increasingly by product pipelines.

A comparison of the range of costs for various types of petroleum transporation based on a long-haul basis is given in table 10. In general, the high prices apply to very small types of equipment or, in the case of trucks, to densely populated areas. Conversely, the lower costs reflect longer hauls and the use of newer, large equipment. In all forms of petroleum transportation, cost reductions have been sought through increase in size, by greater use of automation, and by better design and quality of materials.

TABLE 10—*Representative cost of petroleum transportation*

Type of transportation	*Mills per ton mile*
Tankers	0.5– 2.0
Barges	1.5– 3.0
Pipeline	1.5– 6.0
Tank truck	30 –50
Railroad tank car	30 –70

There were more than 200,000 miles of petroleum pipelines in the United States in 1962. There are 77,000 miles of pipe in crude gathering systems in oilfields. These are generally from 2 to 6 inches in diameter. Another 70,000 miles of pipe are in crude oil trunk pipelines ranging from 6 to 30 inches. There are 53,000 miles of petroleum products pipelines

which extend from refineries to distribution terminals serving most U.S. cities.

The gas utility industry operated over 710,000 miles of pipelines at the end of 1963, which was a gain of approximately 27,000 miles over the pipeline mileage in 1962. Transmission mains totaled over 200,000 miles, distribution mains over 448,000 miles, and field and gathering lines approximately 61,000 miles (*1*).

Prior to the mid–1930's crude pipelines were generally regarded as plant facilities of their refinery owners. Pipelines were of small diameter with a limited capacity. After World War II, the Nation's petroleum demand expanded, and demand continued to increase at an accelerated rate. During this time, pipeline building proceeded rapidly, and improvements in the quality of pipe and in construction methods helped contribute to the development of large-diameter pipeline systems. The capacity of a pipeline increases approximately as the square of the diameter; however, investment and operating costs do not increase nearly so rapidly as the increase in capacity. Large-diameter pipelines were justified by the large volume of crude oil to be moved and by the savings that could be gained. During the past 20 years many of the networks of crude oil lines have been interconnected. The result has been the development of a common carrier pipeline system that allows refiners flexibility in seeking supplies of crude oil from an almost unlimited number of oilfields in many States, and it permits refiners to move products from one area to another.

Water carriers rank second only to pipelines in the volume of petroleum transported. In 1962, the total crude petroleum and products moved in the United States by water carriers was slightly in excess of 2 billion barrels, or 29 percent of the total transported.

In early 1963, the world tankship fleet capacity for oceangoing vessels of 2,000 gross tons and over was 4,543 T–2 equivalent (*4*). The term "T–2" is used as a unit of measure of carrying capacity of tankers and represents a World War II tanker of 16,725 deadweight tons (dwt).

The continued growth in number and size of world tankers in the past decade is related to favorable economic advancements in moving petroleum from the Middle East producing areas to Western Europe and Japan to meet rapid growth in consumption and new energy needs.

The cost of operating a 45,000-dwt tanker is about one third less than that for a T–2 tanker, and the operating cost for an 80,000-ton tanker is about half. Surplus capacity and intense competition have characterized the tanker business. The downward trend in tanker transportation costs is the result of the following: (1) marked decline in tanker construction costs from the high level of the Suez crises; (2) increases in speed which represent time savings of as much as 5 days on some long hauls; (3) substantial improvements in port facilities which reduce time for loading and discharge; (4) reduction in fuel costs (bunker oil prices have declined 20 percent since 1956); and (5) most recently, the application of automatic machinery and centralized control systems by ships under foreign flags.

From World War II to 1956, the United States had the largest tanker fleet in the world. In 1956, the United States had 19 percent of the world total carrying capacity. However, by 1963, the United States ranked fourth (12 percent) because of aggressive and fierce competition from foreign-flag owners. In 1963, Liberia ranked first (17 percent), the United Kingdom second (15 percent), and Norway third (14 percent), respectively.

According to the U.S. Department of Commerce Maritime Administration, effective June 30, 1964, the privately owned fleet of U.S.-flag tankers, and oceangoing steam and motor ships of 1,000 gross tons and over contained 103 tankers. Of these, 87 are medium tankers, 25,000 to 45,000 dwt; 15 are large tankers, 45,000 to 70,000 dwt; and 1 is in the supertanker class, over 100,000 dwt. The largest U.S.-flag tanker is the SS *Manhattan*, a 108,590-dwt tanker with a carrying capacity of about 910,000 barrels of heating oil. This tanker is longer than 3 football fields and as high as a 10-story building.

The most economical forms of bulk petroleum transportation—pipeline and tanker—can obviously be used only where hughe batches of fluids can be placed in storage at destination.

Faster loading facilities and reduction in the evaporation loss during loading have aided tank-truck shipments. The major improvement in tank-car and tank-truck transportation has been that of increase in carrying capacity.

Natural gas is the only fuel transported by pipeline in the gaseous state from source to consumer. Within the past 2 years, experiments in transportation of liquefied methane by refrigerated ships have proved successful, but markets are located that have access to ocean transport. Shipments of liquefied methane are not permitted on inland waterways in the United States for reasons of safety. Liquefied methane carriers are not competitive with pipeline transportation. Hence, seaports on the east coast of this country are served more cheaply by gas pipeline than is possible by seagoing vessels.

Most of the storage of crude oil and petroleum products is in aboveground steel tanks. The principal improvements in oil storage have been

larger size tanks to decrease the cost per unit of volume and increased use and better floating roofs to reduce evaporation losses.

The storage of natural gas at or near major consuming centers to meet peak demands (peak shaving) of short duration has long been practiced by gas utilities. Aboveground low-pressure holders have been in common use by the manufactured-gas industry for many years.

Within the past 20 years underground storage has been developed for LPG. Caverns mined from impervious rock, or washed from salt beds, are used for this purpose and have proved most economical. Natural gas storage near large distribution areas provides a means by which the varying load requirements can be satisfied while providing a more desirable high load factor for pipelines. Reservoirs generally used for natural gas storage are: (1) depleted gas fields; (2) depleted oilfields; and (3) aquifers (porous rock formations similar to oil and gas formations but containing water). Of these, depleted gas and oilfields are the most desirable reservoirs, but they are not available in all areas of the continental United States. Consequently, the search has turned to locating suitable aquifers for prospective storage use, and some of these projects have been used successfully for natural gas storage.

A part of the phenomenal growth of the natural gas industry following World War II has been the great expansion of underground storage of natural gas. The quantity of natural gas in storage reservoirs has more than doubled over the last 9 years, reaching a total of 2,745 billion cubic feet at the end of 1963; an average annual growth of about 9 percent. Most of the natural gas stored in 1963 was in Pennsylvania, Michigan, Ohio, and West Virginia with storage volumes of 491 billion, 471 billion, 376 billion, and 320 billion cubic feet, respectively.

RESEARCH

Industry research covers the entire range of petroleum operations. Efforts are directed to new and improved instruments and techniques for finding new oil-bearing reservoirs and oil deposits, better equipment for drilling wells and better fluids for drilling, better methods for completing wells, and more efficient methods for producing the oil from the oil reservoir. Research is concerned with corrosion problems associated with producing, refining, and storing petroleum and natural gas. Research applied to transportation has achieved significant results, and oil and gas move more economically than almost any other commodity.

The United States now is freed from dependence on imported rubber, and the synthetic rubbers now are far better for major uses than the natural. Military aviation supremacy in World War II was based on the high-octane aviation gasoline developed through research. Research developed processes for increasing the amount of gasoline obtainable from a barrel of crude oil from about 20 percent to over 75 percent, even though gasoline demand does not require over 50 percent. Increased octane number of motor gasoline enables 2 gallons of present fuel to do the work of 3 old lower octane gallons.

High-speed, high-output, internal-combustion engines are the result of research efforts in metals, engine design, and fuels and lubricants. Lubricants have received much attention from petroleum research staffs and have kept pace with engine requirements.

Another outstanding industry development achieved largely from research is the creation and continuing great expansion of the petrochemical industry. Currently, one-half of the total dollar value of organic chemicals produced in the United States is from petrochemicals or derivatives of them.

The cost of petroleum research and development is high. In 1963, the industries and Government in the United States spent $312 million on fundamental research.

During the past 3 years about 20 percent of the petroleum industry's research effort has been devoted to exploration and production, 23 percent on refinery processing methods, 20 percent on petroleum product development, 24 percent on petrochemicals, and 13 percent on other types of research.

The diversity and magnitude of the research effort supported by the petroleum industry is evidenced by the technical manpower employed—about 9,000 professional engineers and scientists, supported by 6,000 technicians, with a total of more than 20,000 persons employed in research and development.

The industry now allocates about 16 percent of its total research expenditures for basic research. The National Science Foundation defines basic research as original investigation for the advancement of scientific knowledge that does not have specific commercial objectives, although it may be in fields of present or potential interest to the suporting company.

The Bureau of Mines has had an active and productive petroleum and natural gas research program for over 50 years. This program has been supported financially in part by State governments, industry and industry associations, and other Federal Government agenices for most of these years. The research of the Bureau and the Department is broad and has a nationwide, and in many ways even a worldwide, view which includes both long- and short-

range activities; its aim is to benefit the Nation by solving petroleum problems relating to its own functions as well as those of other Government agencies and in serving as technical consultant to them on petroleum matters. Many of the problems are such that industry will not or cannot undertake them because of their broad industrywide significance, which would not be attractive to an individual company. Other problems are related to broad technologic areas that are commercially marginal and have only future importance.

The early Bureau of Mines program investigated oil-well cementing, drilling mud, physical properties of hydrocarbons, and detailed petroleum-engineering field studies. Later cooperative research efforts were of great value in understanding and operating oil and gas reservoirs, in high-pressure separation of oil and gas, and in natural-gasoline productions (*3*). Fundamental studies of the properties and composition of oil, gas, and associated fluids and rocks have been a continuing part of the program.

The current research program of the Bureau contains studies involving determination of metallic materials in crude oils to provide efficient processing of crude oil fractions, storage stability of finished products, research on combustion of hydrocarbon fuels in engines and burners, investigations of products of combustion relative to air pollution, studies of new and improved ways to store natural gas, development of computer programs for fluid flow problems in petroleum reservoirs, research on the use of explosives (conventional and nuclear) for stimulating oil and gas production, studies of the use of radioactive tracer application to fluid flow in underground reservoirs, and research on methods to increase ultimate petroleum and natural gas production.

OUTLOOK

Rapid growth in energy demand resulting from an increasing population and expanding economy accompanied by a greater per capita energy consumption indicates that in the next few decades oil and gas will be providing a greater volume as well as a larger share of the world's fuel supply. Free world consumption during this period is forecast to double. In the mid-1960's world consumption of petroleum increased 6 to 7 percent annually, with a 10-percent increase outside the United States and a 3-percent increase in the United States. The present rate of consumption in the United States is 10.5 million barrels per day; within the next two decades consumption is expected to reach 15.6 million barrels per day. The lower rate of growth of oil consumption in the United States is a reflection of a mature economy where the use of oil for fuel is established and widespread. Another major factor for the low growth rate of oil has been a substantial and continuing shift by the consumer from oil fuels to natural gas.

Over five-eighths of the world's proved crude oil reserve is in the Middle East, mainly in the Persian Gulf region. Recent increases in the proved petroleum reserve there have been simultaneous with unusual increases in demand resulting from the expanding economies of many of the previously undeveloped nations. Should present trends in world oil supply continue, petroleum and natural gas will be derived increasingly in the future from offshore oil reservoirs; by liquefaction of natural gas and transporting it as a refrigerated liquid from remote areas to energy markets; and by the production of supplemental fuels obtained from oil shale and bituminous sands when these resources, which are now economically marginal, become more competitive with oil and gas. Exactly what proportions of the oil supply will be produced eventually from these marginal resources, and the timing of such events are at present indeterminate. A substantial part of the technology needed on extraction of oil from oil shale and bituminous sands has been developed, and research and development is still in progress. Success in this work will enable future economic utilization of these vast unused hydrocarbon resources which far exceed known petroleum reserves.

Petrochemical production in the United States will continue to rise and can be expected to be the area of the petroleum industry having the greatest increase in profits. For example, during 1963 the market for polyethylene resins increased 11 percent over the previous year. Approximately 30 million pounds of ethylene-propylene rubber and straight-chain alcohols derived from ethylene were produced in 1963, and a demand growth of about 100 million pounds is forecast within the next 10 to 15 years. By the end of this decade estimates of ethylene-propylene rubber requirements place the increase in ethylene annual demand at 300 million pounds. Although sometimes not considered a petrochemical in the strictest sense, ammonia, one of the fastest growing chemical products, now is predominantly derived from petroleum hydrocarbons.

For the next few decades the petroleum and natural gas industries may expect a continuation of keen competition from other energy sources. Oil, having its inherent advantage in supplying energy for transportation, is almost certain to retain its present superior position. Gas can be expected to win a larger share of the U.S. market in space heating and industrial fuels. The same trends for both oil and gas are expected in Europe, where newly discovered gas supplies are being made available, as both fuels demonstrate their convenience and low cost and establish a record of dependability in price and supply. The short-term outlook for the U.S. oil and gas industries is more favorable than it has been for several years, but the oil industry's present capacity to produce 2.5 million barrels of oil per day in excess of demand will continue to exist for several years.

Natural gas accounts for 98 percent of all gas consumed in the United States and has displaced manufactured gas, which formerly was distributed in most cities. Within the past 20 years, natural gas has exhibited a consistently high growth rate. The average increase has been 5.8 percent per year for the past decade, and future growth to the end of the century is estimated at about 3 to 4 percent per year.

Yearly crude oil demand in 1963 increased 3.3 percent over the demand in 1962. Competition for markets continued to be intense, but the supply of crude oil and products remained at about the consumption level. Crude-oil prices have remained stable in the United States for the last 5 years; this probably will continue because of excess productive capacity. Product prices, especially for gasoline, in general were down to the 1961 level.

Prices of natural gas at the wellhead have increased by about half in the past 7 years, and the average consumer price has increased over 25 percent. Gas prices are expected to remain stabilized because of competition from new energy sources being developed.

Asphalt production and consumption have continued to grow in recent years and are expected to reach recordbreaking marketing years in the immediate future because of the use of asphalt paving in the new Interstate Highway System and the related primary, secondary, and urban highways.

Production of natural-gas liquids (NGL), a coproduct of oil and gas, in recent years has had record gains. Combined with natural gasoline, NGL currently constitute about 10 percent of total new petroleum production. This has resulted from increased oil and natural gas production, especially from deep, high-pressure reservoirs having greater proportions of natural gas and NGL. Both NGL and natural gasoline have been establishing record yearly production totals.

Natural gas has increased its share of the U.S. energy market from 18 percent to about 30 percent in the last 10 to 12 years. In 1963, natural gas provided 42 percent of the industrial fuel consumed. With a sustained exploratory effort the growth in domestic natural-gas production is expected to be adequate to meet anticipated demands in the foreseeable future.

Of prime importance is the development of technology that will enable drilling exploratory wells to greater depths and to produce from them at economic costs; and the solution of problems in offshore operations which will result in extension of these operations farther into the deeper seas on the continental shelves.

PROBLEMS

The U.S. petroluem industry continued its efforts in 1963 to cope with a variety of conditions confronting it in a transition period. Domestic demand for oil, gas, and products has not grown sufficiently to utilize fully the present capacity of producing and refining, both of which are in excess of present market needs. The industry is adjusting its operations to remedy economic ills and achieve a supply-and-demand balance.

The matter of efficiency in operations, although improving constantly, has been achieved only through extensive effort. There has been a large program in all segments of the industry to achieve greater efficiency, and numerous moves to diversify are planned or are underway that involve new industrial, financial, and technological undertakings. New concepts of investment and a vigorous attack on waste are being employed, and more streamlined methods and stringent economies are being exercised.

There are several causes for the current domestic surplus of oil, among which was the decline in the rate of increase in U.S. oil demand following the expanded programs to supply crude petroleum and products for the Korean war effort and the Suez crisis. The rate of increase in demand has declined from 6 percent per year to about 3 percent. Adjustment to this change in trend has been slow because of the necessary leadtime required to change supply program plans that had already been put into operation.

Another important problem facing the industry is financial incentive; that is, the industry's ability to generate capital from oil and gas pro-

duction and then to reinvest it in exploration and development of new reserves. If, for national welfare and security, the 1963 ratio of reserves to annual crude-oil production (11.3:1) is to be maintained, the petroleum industry in the next decade will be faced with the necessity of having to reinvest as much as 65 percent of the capital generated from production on exploration and development. This high level of expenditures exceeds past requirements and is due largely to the continuing increases in the costs of finding and developing new reserves. In view of this, many companies have been diverting capital to operations abroad, where a more favorable economic climate exists for the development-cost to crude-price ratio.

As a consequence, the amount of participation in international petroleum operations by U.S. oil companies has changed substantially during 1955–63. There now are many more American companies in world oil operations than formerly. These companies have been willing to absorb the high initial cost of foreign operations in order to share in the profits of supplying the rapidly growing markets in the free world. These have grown at an annual rate of 6 to 7 percent, as compared with 3 percent for the United States.

There are specific and recognized needs for additional research in practically all segments of the industry.

Basic research should be continued on the origin of oil and its early migration in prehistoric times to provide the information that is needed for the development of new and improved techniques for finding oil and for delineating oilfields after they are discovered. The present cost of exploration activity by the industry clearly is an incentive for research and development. There is a continuing need for more information about the interrelationships of oil, gas, water, and rock in reservoirs. Efforts to improve finding instruments and techniques certainly should be continued. There is a real need for the full assessment of the potentialities of proposed new methods for finding oil and gas without well drilling.

The problem of recovering the maximum amount of oil from a discovered oilfield is as old as the industry itself and has received major attention in the past. The tremendous opportunity in this area demands a continuing and increased effort. Advances are needed to increase production efficiencies in order that the economic time for abandonment of oilfields will be extended and recoveries will be increased.

Some of the largest gains in technology have been in the development of more efficient and economical processing systems and operations. The huge volume of refinery throughputs offer a most attractive target for research and present effort in such activity should continue.

The end result of the total petroleum industry effort is and has been to provide new and better products to the industry's customers, including the development of new products for new customers. The development of aircraft that can fly some two to four times faster than the speed of sound is an example of a need for better and more stable fuels and lubricants that simply were not available in the past. Research that has produced a wide variety of useful petrochemicals has been financially rewarding in the past two decades, and such research in the future will be attractive to researchers and to management. The unique characteristics of hydrocarbon materials offer tremendous possibilities for the development of many more new and better products.

If petroleum and natural gas are to retain their competitive positions in future energy markets, further improvements in geological and geophysical methods will be needed to improve discovery methods. The production segment of the petroleum industry is seeking solutions to its problems through research programs directed toward increased yields from oil and gas reservoirs by the development, improvement, and application of new techniques to drill, complete, and produce oil and gas wells; the perfection of new and improved methods of reservoir stimulation; the application of better techniques for secondary and tertiary recovery; and by making more universal applications of these techniques to producing areas to increase the efficiency of oil recovery. It is necessary that new and more effective low-cost methods be devised to recover the oil that remains in oilfields nearing the economic limit of production by primary means. Petroleum being left underground usually amounts to more than half of the oil originally in the reservoir and sometimes is as high as three-fourths.

Storage of natural gas and natural-gas liquids underground to meet peak demands (peak shaving) has become extensive in the United States, but still is beset by economic and technical problems which restrict its broader use. In gas storage, difficulties exist in selecting underground formations for storage reservoirs which are in suitable geologic strata; are not unduly deep; have favorable permeability, porosity, and other rock properties; and yet lie beneath impermeable strata to prevent leakage. They also should be suitably located with reference to pipelines and markets.

In natural-gas liquefaction there are a number of problems that require solution in both liquefaction-plant practices and liquid-methane carriers. Improvements may be expected to be

forthcoming in the near future from substantial research and development efforts of the industry, here and abroad, and from the experience now being acquired in several actual commercial operations.

Among the most troublesome problems in pipeline transportation are corrosion of steel in pipelines and the high cost of installation, operation, and maintenance. These are continuing problems even though they are being alleviated somewhat in natural-gas distribution by the use of plastic pipe for service to widely scattered customers in small communities. In oil and gas production, plastic pipe and pipe liners are being utilized to an increasing extent for gathering lines, saltwater disposal, and various waterflood applications.

Some cost reductions have been achieved that help, but are only partial solutions of industry problems in oil and gas lines. These include work on the development of improved pipelaying methods, such as better trenching machinery, improved pipe-welding techniques, and the use of high-strength, thin-walled steel pipe and anticorrosion coverings and pipe. Many of the problems remain and much still remains to be done to improve gathering, transmission, and distribution systems through better techniques and materials which will reduce costs.

The drilling segment of the petroleum industry is confronted with problems of portability because of the advancing trend in depth of drilling required, both on land and offshore. To enable these operations to continue at economic levels in this highly competitive business, continued emphasis must be placed on weight reduction and on improved equipment and drilling techniques. Transportation, well-completion costs, and reduced rigging-up time are some problem areas of major concern which offer opportunities for cutting costs.

Refining problems center on cost reduction through improved technology. Basically they involve the need to upgrade raw and intermediate stocks and obtain greater throughput, thereby increasing product quality and yields. The refiner must minimize downtime, off-specification runs, develop new and improved processes, and obtain improved catalysts and rejuvenation methods to achieve more efficient plant and raw-material utilization. In marketing there is a need constantly to develop new products and outlets.

Petroleum hydrocarbons in the last decade have become a widely recognized major source of chemicals, as well as a substantial contributor to the growth of the process industries. However, petrochemicals might be termed "microproducts" in comparison with the usual products from petroleum and natural gas which in this context might be termed macroproducts. The relative output figures are in the ratio of 30 million to 470 million tons per year, respectively. In most instances petrochemicals are coproducts of petroleum refining. They are continuing to attract the interest of oil, gas, and chemical companies, but the petrochemical industry is considered by many to be near the threshold of maturity. This maturity phase is characterized by product-price declines, which have emphasized the need for greater efficiency, better processes, and lower costs. Price declines have focused attention on global economic conditions and markets and the importance of scale of operations on the economics of the industry. The nature of petrochemical production requires a high investment per pound of product, which restricts participants to those having ample financing and marketing outlets.

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PHOSPHATE ROCK

By Richard W. Lewis [1]

DEPOSITS of phosphate rock occur in many countries throughout the world, but the largest known occurrences and those now of greatest economic importance are in North America, Europe, and North Africa.

Phosphate rock is mined chiefly by open pit methods, although eventually more underground mining will be required in the Western field. Most of the Florida and Tennessee rock requires beneficiation before it is utilized by industry. Although beneficiation has not been extensively used in the Western area, it is becoming more important and in 1963 two flotation plants and several washing plants were in operation.

Three fundamental methods are in use for decomposing phosphate rock to obtain products suitable for fertilizer and industrial purposes: (1) Acid treatment; (2) thermal reduction; and (3) thermal treatment without reduction.

The United States, with its huge inferred reserve, has more than enough phosphate rock for its needs. Production capacity is more than adequate for domestic requirements and about 20 percent of production is exported.

Phosphate rock is manufactured into many products for agricultural and industrial uses (*27*). The quantity used domestically for agricultural purposes (about 60 percent of total sales in 1963) has always exceeded that used for all other purposes. Thus, the consumption of phosphate rock largely follows that of fertilizers for which demand increases annually. A continuation of this trend is expected. However, production capacity is continually expanding and it is believed that it will meet any expected increased demand, which may reach 10 million long tons, P_2O_5 content, by 1980.

Phosphate rock is not on the Government list of strategic and critical materials, but elemental phosphorus is an important war material, and phosphatic fertilizers are essential to maintain and expand the agricultural output of the Nation.

Nearly 30 percent of the known reserves of phosphate rock in the world are in the United States. This supply is adequate not only for domestic requirements but also for substantial export. The phosphate-rock industry is concerned with problems of effective utilization of this resource.

BACKGROUND

The phosphate-rock industry in the United States began in 1867 in South Carolina with a production of about 2 long tons of P_2O_5 content. Total U.S. output expanded to about 450,000 tons in 1900, and to nearly 5 million tons in 1958. During the past 5 years production has continued to increase and in 1963, P_2O_5 content of marketable rock produced amounted to more than 6 million tons. From 1867 to 1894, South Carolina was the largest phosphate-rock-producing State. Florida began producing in 1888, Tennessee in 1894, and the Western States in 1906. In Kentucky a small mine began producing in 1919 and operated until 1926. A little over 93,000 tons was mined during its 7 years of operation. Phosphate beds in Independence County, Ark., were mined, starting about 1900 and ending in 1912, but total output amounted to less than 33,000 tons. Interest in Arkansas phosphate was renewed in 1963 and production and sales were reported by one company operating in central Arkansas. Exploitation of an apatite deposit in the Piney River area of Virginia was undertaken in 1937. The ore concentrates were processed into phosphoric acid and monocalcium phosphate until 1943. Defluorinated phosphate rock was produced from 1943 to 1948 when both mine and plant were shut down. Crude phosphate rock was first produced

[1] Commodity specialist.

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in the Western States in 1906 from deposits in southeastern Idaho. Limited production from Wyoming and Utah followed in 1907 and from western Montana in 1923. The industry expanded steadily and in 1963 a production of about 3 million long tons was reported. In 1961 several companies began to explore the development possibilities of the large phosphate deposits in Beaufort County, N.C. One firm, Texas Gulf Sulphur Co., completed test mining and construction of a pilot plant in 1963. Development of the deposit continued in 1964 and the company planned production of 3 million tons annually by 1966.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

In the United States phosphate-rock deposits have been reported in 23 States. A total of 24 companies and the Tennessee Valley Authority (TVA) were producing phosphate rock in Arkansas, Florida, Tennessee, and the Western States—Idaho, Montana, Utah, and Wyoming in 1963. Deposits in North Carolina are being developed and are expected to gain commercial importance in 1965. In the past, phosphate rock has been produced in commercial quantities also in Alabama, Georgia, Kentucky, New Jersey, New York, North Carolina, Pennsylvania, South Carolina, and Virginia.

Most of the present producers beneficiate the ore to a marketable product in washer plants adjacent to the mines. In addition, many producers operate flotation plants for further recovery and upgrading. A few, however, sell the ore to other producers or processors. Also, some ore is sold for direct application to the soil. Most of the major producers manufacture phosphatic fertilizers or elemental phosphorus, usually in plants near the mining operations.

Elemental phosphorus is produced by 6 companies and TVA in 11 plants in 6 States—Alabama, Florida, Idaho, Montana, Tennessee, and South Carolina. There are about 1,400 fertilizer mixing plants dispersed throughout the United States.

Florida has been the leading producing State for many years and is currently furnishing over 70 percent of domestic production, 98 percent of which comes from the land-pebble field. This percentage is expected to drop during the next 10 years with substantial production beginning in North Carolina and increased production in the Western States. The following producing companies are listed in decreasing order of current output: International Minerals & Chemical Corp. (IMC); the American Agricultural Chemical Co. (AAC); V–C Chemical Co., Division of Socony Mobil Oil Co. (V–C); American Cyanamid Co.; Davidson Chemical Division, W. R. Grace & Co.; Swift & Co.; Armour Agricultural Chemical Co.; Smith-Douglass Co., Inc.; and New Concept Co. All of these firms except New Concept Co. manufacture phosphoric acid and superphosphates in plants, most of which are adjacent to their beneficiation facilities. Elemental phosphorus is produced in Florida by AAC, Victor Chemical Works, and V–C. Florida hard-rock is mined, washed, and dried by Kibler-Camp Phosphate Enterprise. The remainder of Florida's output comes from the soft-rock field, where four companies mine, dry, and sell soft-rock for direct application, fertilizer filler, and stock and poultry feed.

In Tennessee the following companies, which also produce in Florida, mine, beneficiate, and dry phosphate rock, and either manufacture fertilizer locally or ship the rock to their fertilizer plants in other areas: Armour Agricultural Chemical Co., IMC, and V–C. Monsanto Chemical Co., Victor Chemical Works, and Hooker Chemical Corp. produce beneficiated phosphate rock as a raw material for their elemental phosphorus plants in Tennessee. TVA mines phosphate rock in Tennessee for use in its phosphorus furnaces at Wilson Dam, Ala. TVA also purchases land pebble and other phosphate rock at various intervals for its experimental work. In addition, several smaller concerns have mined and sold phosphate rock in Tennessee periodically. M. C. Boyle Phosphate Co. was the only small firm operating in 1963.

In 1963, Central Farmers Fertilizer Co., Monsanto Chemical Co., and J. R. Simplot Co. were producing in Idaho. Montana Phosphate Products Co., George Relyea, and Victor Chemical works were mining in Montana, and San Francisco Chemical Co. mined and beneficiated phosphate rock in Utah and Wyoming. Elemental phosphorus is produced in the Western field by Monsanto Chemical Co. at Soda Springs, Idaho, FMC Corp. at Pocatello, Idaho, and Victor Chemical Works at Silver Bow, Mont. J. R. Simplot Co., a producer of phosphatic fertilizers in Idaho, supplies the phosphate rock to FMC for its furnace operation. Central Farmers Fertilizers Co. produced elemental phosphorus at its Georgetown, Idaho plant for several years but the furnace was shut down in 1963. The entire output of Montana Phosphate Products Co., a subsidiary of Consolidated Mining & Smelting Co., of Canada, Ltd., was exported to Canada where it was processed into fertilizer and the bulk shipped back into the United States for consumption.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

"Phosphate rock" is a commercial term for a rock containing one or more phosphate minerals, usually calcium phosphate, of sufficient grade and suitable composition to permit its use, either directly or after concentration, in manufacturing commercial products. The term "phosphate rock" includes phosphatized limestones, sandstones, shales, and igneous rocks.

Chemical analyses usually are reported as percent P_2O_5 or tricalcium phosphate ($Ca_3(PO_4)_2$) also known as B.P.L. (bone phosphate of lime) (1.0 percent tricalcium phosphate (B.P.L.) = 0.458 percent P_2O_5).

Ordinary superphosphate is the product made by mixing phosphate rock with sulfuric acid. Triple superphosphate, sometimes called treble superphosphate, is the product made by mixing phosphate rock with phosphoric acid.

TECHNOLOGY

Geology and Occurrence of Domestic Deposits

Phosphate rock does not have a definite chemical composition. The major phosphorus minerals of most phosphate rock are in the apatite group and can be represented by the formula $Ca_5(PO_4)_3(F,Cl,OH)$. The PO_4 radical can be partly replaced by small quantities of VO_4, AsO_4, SiO_4, SO_4, and CO_3. The (F, Cl,OH) radical may be all fluorine, chlorine, or hydroxyl ion or any combination thereof. Also, small quantities of calcium may be replaced by many elements, such as magnesium, manganese, strontium, lead, sodium, uranium, cerium, and yttrium. The major impurities include iron as limonite, clay, aluminum phosphates, fluorine, and silica as quartz sand (*17*).[2] Phosphate rock occurs as nodular phosphates, residual weathered phosphatic limestones, vein phosphates, and consolidated and unconsolidated phosphatic sediments.

Florida.—(*2*, *3*, *5*) Hard-rock phosphate occurs in localized deposits from a few inches up to 100 feet thick, overlain by 10 to 50 feet of overburden and irregularly distributed in an ore composed of sand, clay, and soft phosphate. The deposits range from areas of less than 1,000 square feet to several acres; high-grade masses contain less than 1 ton to several tons. In the workable deposits the hard-rock phosphate forms 25 to 30 percent of the material. The hard rock is usually lightcolored and dense and has a phosphate content up to about 38 percent P_2O_5.

The main body of commercial land-pebble phosphate rock occurs as an unconsolidated phosphate-rock ore, and in the operating fields averages 30 feet in thickness, with an overburden 5 to 20 feet thick. The grade of ore is not uniform but averages 15 percent P_2O_5. The phosphate rock recovered ranges from plus 14-mesh pebbles to particles as fine as 200-mesh. Most of the phosphate rock contains 30 to 32 percent P_2O_5 after beneficiation.

In addition, soft phosphate rock, a tan or gray colloidal phosphatic clay containing variable quantities of P_2O_5, commonly is associated with both the land-pebble and hard-rock phosphate deposits.

Tennessee.—Three types of phosphate rock—brown, blue, and white—occur in Tennessee. Almost all the Tennessee production has been brown-rock phosphate.

The brown rock is the product of weathering and leaching of phosphatic limestones and overlies the parent phosphatic limestones. In some places the brown-rock deposits are exposed; elsewhere they are covered by clay and soil, usually less than 20 feet thick. Brown rock occurs as bedded deposits, some of which contain substantial quantities of plate and lump rock, but much of that mined since 1945 has consisted of loose, rounded grains of calcium phosphate intermixed with siliceous material. Although designated as brown rock, the color may range from white to dark brown. The brown-rock beds average 22 percent P_2O_5 and do not exceed 32 percent; workable low-grade material ranges between 16 and 24 percent P_2O_5. Much of the rock is beneficiated by washing and screening, but substantial quantities of run-of-mine material are utilized by blending with higher grades.

The blue rock is an unaltered phosphatic shale or sandstone from a few inches to 4 feet thick and averaging 29 percent P_2O_5. Because of its limited quantity and mode of occurrence blue-rock phosphate does not have commercial importance.

White-rock phosphate is of secondary origin; it results from chemical replacement and occurs in scattered pockets with varying P_2O_5 content.

Western States.—The Western phosphate field includes the deposits in Idaho, Montana, Utah, and Wyoming (*8*, *23*). In this region the phosphate rock lies in beds at two geological horizons, the Permian and the Mississippian. Thus far most of the production has come from the Permian deposits. The region has been intensely folded and faulted and then eroded, exposing the higher grade, phosphate-bearing

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

strata in narrow bands along the flanks of folds or along the borders of the faulted areas. The beds dip from horizontal to vertical (*15, 23*).

The currently economic Permian phosphate-bearing formation is of marine origin. The phosphate beds are contained in the phosphate shale member of the Phosphoria formation, which is 75 to 180 feet thick and consists of yellowish to brown phosphatic shales, brown to black limestone beds, and one to three economically valuable beds of gray, brown, or black oöitic phosphate rock. The fertilizer grade phosphate-rock beds are 3 to more than 7 feet thick, and the P_2O_5 content is 26 to over 36 percent. Furnace-grade rock, 20 to 26 percent P_2O_5, occurs in beds 10 to 50 feet thick.

Mining

Phosphate rock is mined by open pit methods in all three producing fields—Florida, Tennessee, and the Western States. Underground mining is limited to the Western States.

In the Florida land-pebble deposits the overburden is stripped and the ore mined by large, electric, dragline excavators equipped with buckets, ranging in capacity from 8½ to 34 cubic yards. The ore is slurried and pumped to the washing plant, in some instances several miles from the mines. In the other Florida deposits, the Tennessee field, and the open pit mines in the Western field, the ore is mined by smaller dragline excavators or shovels and trucked to the plants.

Top slicing, sublevel stoping, and open stoping methods used in the Western underground mines are designed to recover the high-grade beds containing a minimum of 31 percent P_2O_5. Large tonnages of material, 20 to 31 percent P_2O_5, are not recovered.

Washing and Beneficiation

Nearly all Florida and Tennessee phosphate-rock ore must be treated before utilization. Washing is accomplished by sizing screens, log washers, various types of classifiers, and mills to disintegrate the large clay balls. The fine slime, usually minus 200-mesh, is discarded. In the Florida land-pebble field the plus 14-mesh material is dried and marketed as high-grade rock or blended with the fine granular material (minus 14, plus 200-mesh) that has been treated in flotation cells, spirals, cones, or tables.

Losses in washer and flotation operations range from 40 percent of the P_2O_5 in the Florida land-pebble field to more than 50 percent in some Tennessee areas. The discarded material, usually minus 200-mesh, contains substantial quantities of phosphate minerals and not only entails the loss of a valuable resource but its disposal constitutes an additional expense (*26*). Many hundred acres of land are occupied by old ponds, and additional pond areas are being acquired for current operations at high cost. Washer slime is discharged as a pulp, with only 4 to 6 percent solids. The pulp is discharged to slime ponds, where an initial settling occurs, and a substantial quantity of relatively clear water is returned to the mining and washing operations. Nevertheless, after settling for 2 years slimes contain only about 25 percent solids. The solids contain 15 to 17 percent P_2O_5—nearly the same as in the original ore.

A large part of the Western field phosphate-rock production is of suitable grade as it comes from the mine. Siliceous phosphate-rock ore and mixtures of phosphate rock and clay minerals are amenable to beneficiation, and in 1958 four companies in the Western field were beneficiating or planning to beneficiate part of their production. Two flotation plants and several washing plants were in operation in 1963. No economic processes have been developed to treat ores high in calcite or other carbonates.

Processing (*11, 28, 30*)

Methods.—There are three fundamental methods of decomposing phosphate rock to obtain products suitable for fertilizer and industrial purposes—acid treatment, thermal reduction and thermal treatment without reduction.

1. In the acid treatment phosphate rock is mixed with sulfuric, phosphoric, or nitric acid or a combination of the three.

Decomposing phosphate rock with sulfuric acid produces either ordinary superphosphate or phosphoric acid. When ordinary superphosphate is wanted, enough sulfuric acid is added to high-grade phosphate rock to convert the phosphate into water-soluble or available monocalcium phosphate. Calcium sulfate also is produced but is not separated from the mixture, which seldom contains over 20 percent available P_2O_5. To produce phosphoric acid, additional sulfuric acid is added, and the phosphoric acid is filtered from the insoluble calcium sulfate.

Acidulating phosphate rock with phosphoric acid produces triple superphosphate. Also, phosphoric acid may be combined with potash and/or ammonia to produce highly concentrated fertilizer salts, such as ammonium phosphates and potassium phosphates.

Nitric acid or a combination of nitric and another acid for acidulation of phosphate rock has not been used extensively in the United States. The resulting product, because of the hygroscopic calcium nitrate content, must be treated further, usually by ammoniation, to produce a suitable fertilizer product. Future

use of nitric acid processes will depend on the availability and relative cost of nitric and sulfuric acids.

2. The thermal-reduction method is based upon the smelting of phosphate rock with carbon (coke) and a siliceous flux in electric or blast furnaces. The products are elemental phosphorus, ferrophosphorus, carbon monoxide, and a calcium silicate slag. The phosphorus is volatilized, condensed, and collected under hot water as a liquid. The calcium silicate and ferrophosphorus are periodically tapped from the furnace. Carbon monoxide is utilized as a fuel, usually in preparing the furnace charge.

3. The three variations of thermal treatment without reduction are: (a) Heating phosphate rock with an alkali salt (for example, Na_2CO_3) with or without substantial defluorination; (b) heating phosphate rock with silica or a small quantity of phosphoric acid in the presence of water vapor to defluorinate the rock as completely as possible; and (c) fusion of phosphate rock mixed with magnesium silicate (serpentine or olivine). After grinding, these products do not require further treatment.

Choice of Processing Method.—The use of phosphoric acid derived from elemental phosphorus in the fertilizer industry has been retarded because of its higher cost, compared with the cost of wet-process phosphoric acid. The food, chemical, and drug industries require acid of high purity and utilize most of the electric-furnace product. Limited quantities of this acid, however, are now used in fertilizers, mainly liquid fertilizers.

Ordinary superphosphate is the simplest phosphate product to manufacture and therefore has been the most widely used. It is largely water soluble, and the phosphorus is readily available to crops when applied to acid, alkaline, or neutral soils. Ordinary superphosphate usually is manufactured close to the market and sometimes is hauled directly from factory to farm in bulk to reduce handling costs.

During the past 5 years, emphasis has changed to the use of higher analysis fertilizers and the production and sales of triple superphosphate in 1963 were equal to those of ordinary. Processes for manufacturing triple superphosphate and other derivatives of phosphoric acid, such as ammonium phosphate, are more complex than the ordinary superphosphate process and require a larger investment. The products carry a far greater proportion of plant food, which tends to offset the higher production costs (*11*, *21*).

Elemental phosphorus is more concentrated than any of the phosphorus derivatives, which results in lower freight cost per unit of P_2O_5. The thermal-reduction method requires a larger investment than the acid or wet process but has the advantage of yielding concentrated products of high-purity suitable for use in the food, chemical, and drug industries, as well as the fertilizer industry.

USES

Phosphate rock has diverse agricultural and industrial uses. The quantity used domestically for agricultural purposes (76 percent of the total sold or used, excluding exports in 1963) has always exceeded that used for all other purposes. Although a substantial quantity of finely ground phosphate rock is applied directly to the soil, particularly in Midwestern States, by far the greater part used for agricultural purposes is manufactured into superphosphate and triple superphosphate.

Elemental phosphorus and phosphoric acid are used to make inorganic and organic chemicals, which are employed as leavening agents, water-softeners, cleansing products, soaps, detergents, plasticizers, and insecticides and for many other purposes. Elemental phosphorus is used for military smokescreens and incendiary bombs, pesticides, and phosphorus alloys. Phosphoric acid also is used in producing fertilizers, animal-feed supplement, beverages, ceramics, as a catalyst and oil-refining agent, in photography, and in dental and silicate cements.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Virtually all domestic phosphate rock contains an average of over 3 percent fluorine combined as fluorapatite. An appreciable part of the fluorine is volatilized during processing creating an air pollution problem as well as a waste of a resource. Most of the fluorine is prevented from escaping into the atmosphere but only a limited quantity is currently recovered for marketing, the remainder is neutralized and discharged as waste (*9*). Owing to the very large tonnage of phosphate rock processed annually, the entire domestic market for fluorine compounds could be more than satisfied if all fluorine was recovered and processed into a salable byproduct.

Florida and Western phosphate-rock deposits contain 0.1 to 0.4 pound of uranium per ton. In 1963, nearly 500,000 pounds of uranium could have been recovered as a byproduct. Several pilot plants operating in the 1950's demonstrated that uranium could be recovered (*7*). Three commercial plants operated on a limited basis, making their final shipments in 1958.

The phosphate deposits of the Western States contain 0.07 to 0.4 percent vanadium oxide

(V_2O_3). Technically feasible processes have been developed for recovering vanadium during the manufacture of phosphoric acid by the wet-process. In the electric furnace process for the production of phosphorus, the vanadium as well as other metal impurities concentrates in the ferrophosphorus which is also a byproduct. Methods for extracting vanadium from ferrophosphorus have been developed (*1*). Two plants were operating intermittently in 1963, one at Salt Lake City, Utah, and one at Soda Springs, Idaho.

Other recoverable byproducts from the processing of phosphate rock include: Calcium sulfate from wet-processing and calcium silicate slag, ferrophosphorus, and carbon monoxide from furnace-processing.

Phosphate rock, potash, and nitrogen are considered the basic fertilizer elements. Thus, changes in the general use of fertilizers will reflect in similar changes in the demand for phosphate rock.

ALTERNATE MATERIALS

There is no substitute for phosphorus as a plant-food element. Basic slag, a byproduct of bessemer or basic open hearth steel manufacturing, however, is an important source of agricultural phosphorus in countries that do not have ample deposits of phosphate rock. Guano and bone meal are also used for their phosphorus content.

Phosphorus compounds used in products other than fertilizers, such as foods, synthetic detergents, and fire extinguisher compounds, frequently can be replaced by other materials at a sacrifice of quality or at increased cost. For example: Soda-ash, borax, soaps, and other cleaning compounds can be used in place of phosphate synthetic detergents, the largest single nonfertilizer product. Similarly, alums may be susbstituted for monocalcium phosphate monohydrate as a leavening agent in baking powder.

RESERVES

Domestic and world reserves and resources tables 1 and 2 have been revised in accordance with the most recent available data.

The reserve of 3 billion tons in the Western field has been estimated to contain one-fourth acid-grade rock (greater than 31 percent P_2O_5) and three-fourths furnace-grade rock (24 to 31 percent P_2O_5). Phosphate rock of commercial grade and minable thickness occurring below entry level is included as a potential resource. A large tonnage of lower grade phosphatic material in the Western field is not included in resources. More detail on the Western phosphate industry and resources has been published recently (*23*). The Florida and Tennessee potential resources include the low-grade minable material.

Only the more important foreign reserves and resources are listed in table 2. Many other countries have minor deposits of phosphate rock, some of which are being exploited. Reserve tonnages, however, in most instances have not been published.

TABLE 1.—*Reserves and potential resources of phosphate rock in the United States* (*14*)

[Million long tons]

Source	Total reserves		Potential resources	
	Marketable product	P_2O_5 content	Marketable product	P_2O_5 content
Arkansas			20	5
Florida	2,040	660	23,350	4,932
North Carolina	[1] 2,000	[1] 600	[2]	[2]
South Carolina			9	2
Tennessee	80	12	5,398	1,129
Western field [3]	3,000	870	20,000	5,800
Total (rounded)	7,100	2,100	49,000	12,000

[1] Estimate.
[2] Data not available.
[3] Includes Idaho, Montana, Utah, and Wyoming.

TABLE 2.—*World reserves and potential resources of phosphate rock and apatite*

Country:	*Million long tons of P_2O_5*
French Morocco	21,000
United States	14,500
U.S.S.R.	7,600
Tunisia	2,000
Algeria	1,000
Brazil	600
Peru	450
Egypt	200
Togo	120
Spanish Sahara	100
Islands of Pacific and Indian Oceans	40
Senegal	40
Other countries	700
Total	48,350

CONSERVATION PRACTICES IN PRODUCTION

In the Western field, when it is necessary to strip low-grade phosphate beds (10 to 18 percent P_2O_5) to recover the underlying phosphate rock, several producers segregate the low-grade material for possible future use.

The phosphatic slimes from the washing plants in the Florida land-pebble and Tennessee brown-rock fields, containing 12 to 15 percent P_2O_5, are discharged into waste ponds. The slimes can be recovered if economic processes are developed to recover the P_2O_5 content or otherwise utilize the slimes.

SOURCES OF STATISTICAL INFORMATION

Statistics for phosphate rock and related industries are collected by the U.S. Department of Agriculture, Bureau of the Census, and Bureau of Mines. Data on crude production, marketable production and value, stocks, shipments by grade, and shipments by uses are collected semiannually by the Bureau of Mines, and 12-month data are published for years ending June 30 and December 31. Data on imports and exports of crude phosphate rock and production of certain phosphate fertilizers and chemicals are collected by the Bureau of the Census. A canvass on the consumption of phosphatic fertilizers, as measured by dealers shipments, is conducted semiannually by the Department of Agriculture and published for years ending June 30.

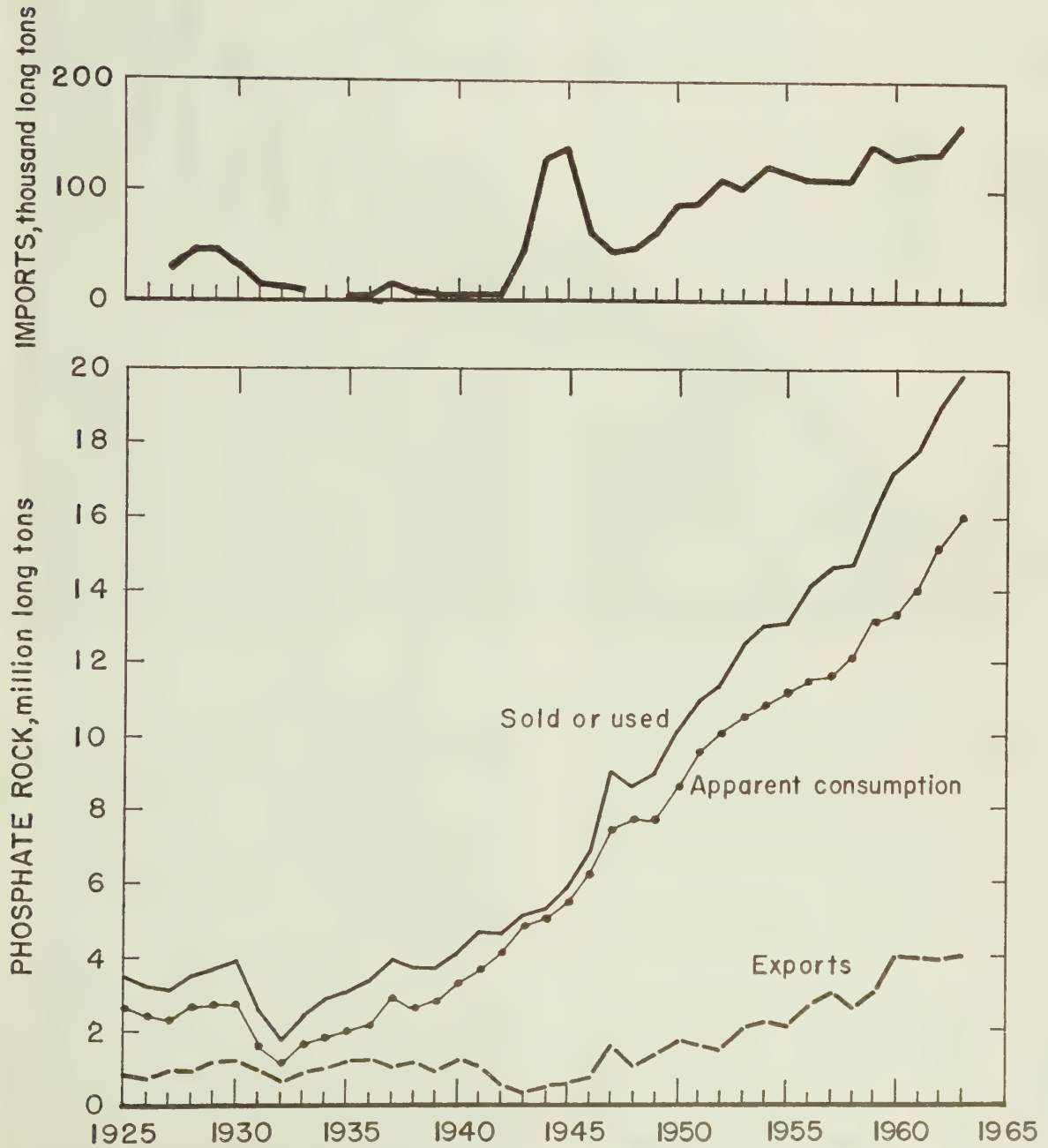

FIGURE 1.—Imports, Sold or Used, Apparent Consumption, and Exports of Phosphate Rock in the United States.

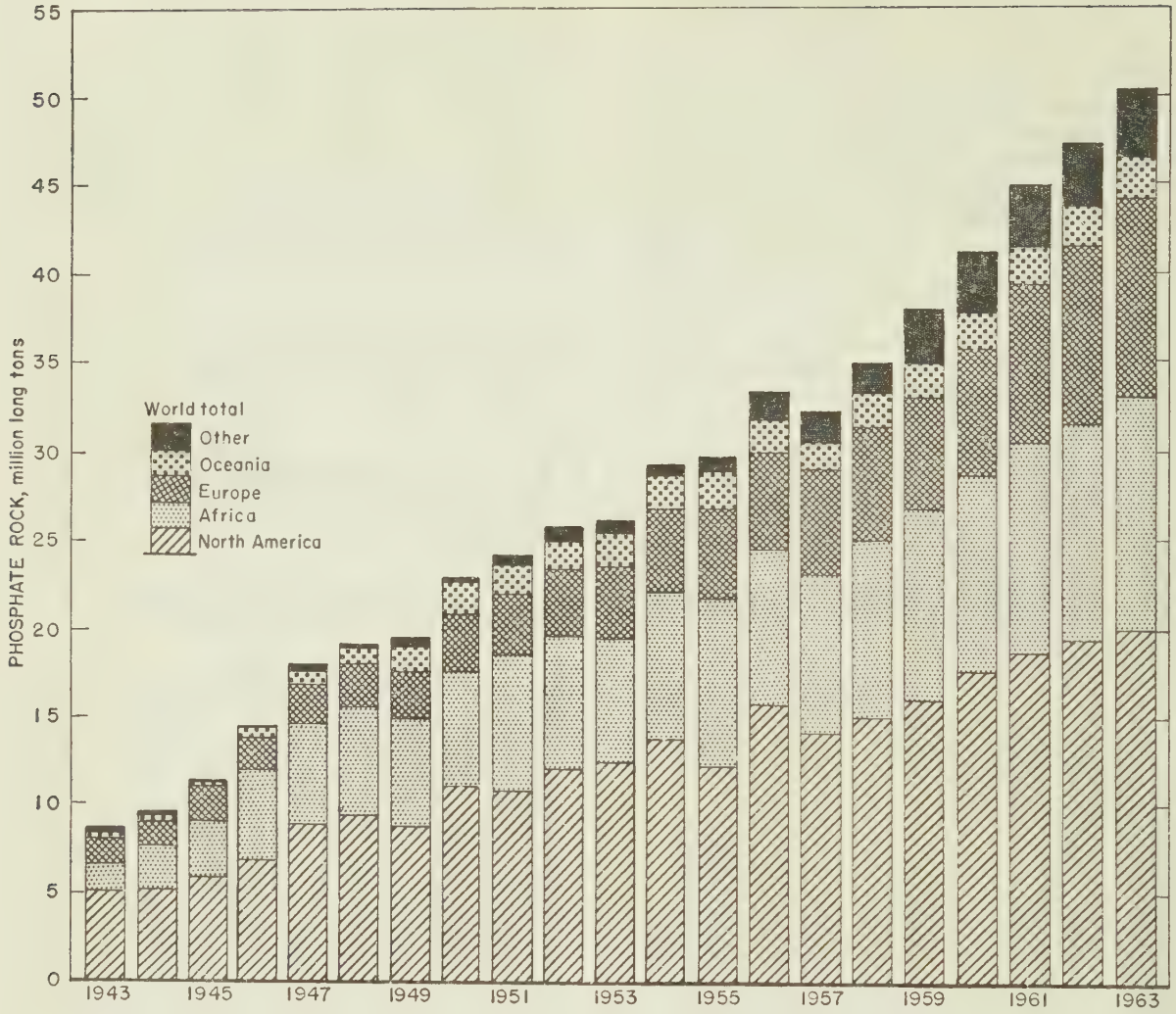

FIGURE 2.—World Production of Phosphate Rock.

PRODUCTION, CONSUMPTION, AND TRADE

U.S. imports, marketed production, apparent consumption, and exports of phosphate rock from 1925 to 1963 are shown in figure 1. World production of phosphate rock from 1943 to 1963 is shown in figure 2.

Of the 19.8 million long tons of phosphate rock produced in the United States in 1963, 74 percent came from Florida, 14 percent from the Western States, and 12 percent from Tennessee. In 1963 no phosphate rock was produced from public domain in Florida. The major part of the 1963 production from the Western States was from public domain and Indian lands.

There is no tariff on crude phosphate rock, apatite, guano, basic slag, or other phosphatic fertilizer and fertilizer materials. Phosphates for animal feed, including ground phosphate rock, have a duty of 10 percent ad valorum. Dicalcium phosphate has an import duty of 9.5 percent ad valorem. All other phosphate chemicals are subject to a tariff with varying amounts of duties.

STRATEGIC CONSIDERATIONS

The United States has ample reserves to supply the domestic requirements at a reasonable projected rate of consumption for several hundred years. The industrial production capacities are expected to keep pace with demand. The needs for low-fluorine phosphate rock, most of which at the present is imported from Curacao, can be met by increasing the plant production facilities for defluorinating domestic rock.

TABLE 3.—*Marketable production of phosphate rock in the United States, by States*

[Thousand long tons]

Year	Florida [1]		Tennessee [2]		Western States [3 4]		Total United States	
	Rock	P_2O_5 content	Rock	P_2O_5 content	Rock	P_2O_5 content	Rock	P_2O_5 content
1954–58 (average)	10,410	3,448	1,700	443	2,028	555	14,138	4,446
1959	11,564	3,794	1,755	458	2,550	687	15,869	4,939
1960	12,321	4,052	1,939	506	3,256	885	17,516	5,443
1961	13,789	4,531	2,235	575	2,535	698	18,559	5,804
1962	13,949	4,543	2,418	638	3,015	823	19,382	6,004
1963	14,592	4,818	2,352	612	2,891	785	19,835	6,215

[1] Salable products from washers and concentrators of land pebble and hard rock, and drier production of soft rock (colloidal clay).
[2] Salable products from washers and concentrators of brown rock, brown-rock ore (matrix) used directly, blue rock, and white rock in 1954–58.
[3] Mine production of ore (rock), plus a quantity of washer and drier production.
[4] Includes Arkansas (1963), Idaho, Montana, Utah, and Wyoming.

Phosphate rock itself is not on the Government list of strategic and critical materials, but elemental phosphorus is an important war material; phosphate chemicals are essential to many vital industries; and phosphatic fertilizers are essential to maintain and expand the agricultural output of the United States. Electric furnaces for producing elemental phosphorus in the United States are meeting all demands for elemental phosphorus for military and industrial use.

GOVERNMENT PROGRAMS

In 1908, soon after phosphate-mining operations were begun in the Western States, about 7,000 square miles of phosphate-bearing public lands in that field was withdrawn from entry, pending examination and classification. In 1910 phosphate-bearing lands in Florida first were withdrawn for investigation and classification.

The Bureau of Land Management, U.S. Department of the Interior, administers leasing of phosphate public lands under Public Law 146—Act To Promote the Mining of Coal, Phosphate, Oil Shale, Gas, and Sodium on the Public Domain (Mineral Leasing Act, Feb. 25, 1920, 41 Stat., ch. 85, sec. 9, pp. 440–441).

The Federal Geological Survey is responsible for mapping the phosphate lands, for certifying to the Bureau of Land Management parcels of land known to contain economic phosphate deposits, and for supervising mining practices to prevent waste and to conserve currently uneconomic resources for future recovery.

The Bureau of Land Management, on application from a qualified citizen or corporate group, opens specified parcels of land to competitive bids for leases if the Geological Survey has certified them to be phosphate bearing or may accept a noncompetitive bid for a prospecting lease on parcels on which no phosphate is certified.

There are no standard provisions regarding phosphate leases. Rents, royalties, and minimum-expenditure requirements are suggested by the Geological Survey, but royalties must not be less than 2 percent of the gross value of output of phosphate rock from the mine. The minimum expenditure requirements usually are nominal, to insure good faith of the lessee, before production is begun.

PRICES

Prices for phosphate rock are based upon the tricalcium phosphate, $Ca_3(PO_4)_2$ (B.P.L.) content in percentage. Maximum limits of allowable iron and aluminum oxides are specified. Bonuses are paid and penalties assessed for variations above and below the base grade. Prices now are quoted in dollars per short ton after years of being quoted per long ton. This change took place on December 14, 1959, in the Oil, Paint and Drug Reporter.

Price quotations for Florida land-pebble phosphate rock from the Oil, Paint and Drug Reporter of January 7, 1963, and December 30, 1963, are given in table 4. The trade journals do not publish quotations for Tennessee or Western States phosphate rock. Price changes largely reflect the cost of fuel oil and labor. Much of the phosphate rock is sold on contract with price quotations used only as a guide.

TABLE 4.—*Prices of Florida land pebble, unground, washed, and dried phosphate rock, in bulk, carlots, at mine, in 1963*

[Per short ton]

Grade (percent B.P.L.)[1]	Jan. 7	Dec. 30
66 to 68	$5.385	$5.38
68 to 70	6.245	6.24
70 to 72	6.825	6.82
74 to 75	7.725	7.72
76 to 78 [2]	8.615	8.61

[1] Bone phosphate of lime, $Ca_3(PO_4)_2$.
[2] Percent changed to "76 to 77" July 15, 1963.

The average values at the mines of marketable production in 1963, by States and types of rock, as calculated from reports by the producers to the Federal Bureau of Mines, were as follows:

State and type: Florida:	*Average value per long ton at mines*
Land pebble	$7.01
Soft rock	8.11
Hard rock	9.48
Tennessee	7.64
Idaho	5.76
Other Western States	8.53

The Idaho value is a composite of the value of high-grade rock and electric-furnace-grade phosphatic shale. Other Western States include Montana, Utah, Wyoming, and a small production from Arkansas.

TRANSPORTATION

Much of the Florida phosphate rock used for manufacturing fertilizer is shipped by boat to the east and gulf coast centers. Florida soft rock, other Florida rock for inland manufacturing centers, and Tennessee and western phosphate rock all move by rail. Truck haulage is not used except locally.

The importance of transporting crude phosphate rock from the producing areas to the fertilizer manufacturing centers has decreased during the past several years. The trend is to manufacture high-analysis fertilizers in the phosphate-rock-producing areas and ship directly to the dealers or consumers, making the cost per unit of plant food cheaper to consumers.

RESEARCH

Both industry and the Federal Government are continuously engaged in research which either directly or indirectly is associated with phosphate rock.

Research by industry has been active particularly in the areas of ore beneficiation and manufactured fertilizers. Most of the larger firms maintain research staffs and laboratories.

The Geological Survey studies the geology of various regions in the United States, determines the phosphate-bearing areas on public lands, and evaluates ore deposits to estimate mineral reserves. Several publications related to studies of phosphate rock occurrences are included in the list of references.

The Federal Bureau of Mines is conducting research to develop an economic flotation method for the recovery of acid- or furnace-grade concentrates from marginal ores of the Western field. A report on a petrographic study of these ores as a part of this project has been published (*13*). Continued investigations are underway to find a feasible method for dewatering the Florida and Tennessee phosphate rock waste slimes. The results of some of these studies have been published (*6*, *24*). Mining research is conducted with an objective to develop lower cost mining techniques to enable the economic recovery of phosphatic shales. An experimental phosphate rock planer was developed and the results of testing were encouraging in longwall-mining of underground beds (*10*, *22*). Additional tests with some alterations made on the planer are scheduled.

In addition, the Bureau scientists are working to develop a method for extracting phosphorus as well as vanadium from ferrophosphorus which is a byproduct from the electric furnace production of elemental phosphorus.

In 1933, TVA was established by an act of Congress, and soon undertook a fertilizer program comprising research, development, design, mining, production, and other phases of the fertilizer industry. The primary purpose of the research and development operations at Muscle Shoals is to provide new and improved fertilizers for the use of the Nation's farmers. The various fertilizers produced in the experimental operations are used chiefly in educational programs in cooperation with land-grant colleges, fertilizer manufacturers, and dealers. A large number of royalty-free, nonexclusive licenses have been issued to fertilizer producers to use TVA patented processes and equipment. TVA has been quite active in recent years with technological developments in the production and use of higher analysis plant foods.

The U.S. Department of Agriculture has been conducting fertilizer-technology research for over 45 years. The Soil and Water Conservation Research Division and its predecessor units have been responsible for the department's fertilizer-technology research since 1911, when this work was first placed on a continuing basis in the former Bureau of Soils. The division maintains close contact with Federal, State, and private agencies interested in fertilizer resources, technology, production, and use, as well as with industry associations, companies, and individuals. These contacts include studies and cooperative investigations. Since 1929 the Department of Agriculture has directed its efforts chiefly toward (1) converting ammonia, phosphoric acid, and potash into high-analysis compounds for fertilizers; (2) improving the processing of phosphate and potash raw materials; (3) developing suitable high-analysis mixed fertilizers; (4) evaluating fertilizer materials and mixtures as plant food; and (5) continuing the study of production, consumption of plant food, and trends in fertilizer use (*4*).

OUTLOOK

It is estimated that the demand for phosphate rock in the United States will increase gradually to about 12 million tons (P_2O_5 content) annually by 1980.

The basic factors affecting the increased use of phosphate rock are: Population growth; higher standards of living; increased knowledge of the benefits of high-analysis fertilizers, both at home and abroad; and advancement in technology of the use of phosphorus compounds in the chemical and metallurgical industries. Land is being continually removed from agricultural production which leads to the use of more fertilizer to compensate for this reduced acreage.

Large increases in the consumption of phosphatic fertilizer by the underdeveloped nations are expected. Foreign phosphate production has been increasing and is likely to continue to do so; however, consumption in other countries will probably tend to exceed foreign production in greater proportions than in previous years, due chiefly to greater knowledge of the benefits from the use of fertilizers. Hence, increased exports of phosphates from the United States can be anticipated, provided world competitive and economic conditions remain favorable.

The demand for elemental phosphorus to manufacture chemicals for industrial purposes should become greater as new uses are continually being discovered. Certain metal phosphides and alloys show promise of increasing use in the field of special construction materials.

Domestic reserves are available to supply several times this expected demand and total resources are believed to be adequate for several hundred years. In addition to the ore bodies presently being mined, substantial phosphate rock deposits in the vicinity of central Arkansas and along the Pamlico River in North Carolina are being explored and developed.

Mining and processing capacities will be expanded to meet the anticipated increased demand. Exploration, development, and improvement of beneficiation techniques can be expected to maintain reserves ahead of mining.

The Florida land-pebble field will increase production slowly but steadily with present producers increasing their mining and plant capacities. Improved and new beneficiation methods may lead to the recovery of the phosphate content of the minus 200-mesh material now being discharged as waste in the Florida land-pebble field and in the Tennessee brown-rock area. This could prolong the life of these reserves by about 25 percent.

The production of phosphate products will increase more rapidly in the Western States since they have about 60 percent of the Nation's known phosphate rock reserves and a large potential market. Open pit mining reserves are large but topography, depth of overburden, and dip of the phosphoria deposits dictate that more and more underground mining will become necessary. Improved methods and larger operations, however, may extend the open pit reserves.

PROBLEMS

Much of the Western States' phosphate rock reserve eventually will need to be mined by underground methods. Present technology will permit only the high-grade ore to be extracted profitably by such methods. Improved techniques must be developed to recover the lower grade phosphatic ore and permit better utilization of this large resource (*29*).

Both open pit and underground mining operations would be more efficient if the information on the grade of the ore and of the tonnage available were more precisely known. Numerous sampling problems exist in obtaining accurate determinations of the grade and reserves. These problems need to be solved as an aid to the improvement of mining technology.

One of the biggest operating problems in exploiting the Florida deposits is the disposition of the slimes. About 30 percent of the mined ore matrix is slime material which is removed in the washer plant and discarded into ponds. The slimes occupy approximately 50 percent more volume than the original phosphate matrix mined. Thus, even though a mined-out pit is used for their storage, one-third more volume is required and must be provided for by the construction of expensive earthen dikes or dams. This constitutes a costly and unsightly storage problem. In addition, the recovery of the water from phosphate slimes for reuse presents another problem of great magnitude. It is complicated by the fact that dewatering must be accomplished at a cost of a few cents per ton in order to be economically satisfactory.

Control of fluorine is a serious operating problem. All phosphate rock ores contain fluorine, some as much as 4 percent. In either the wet or the electric-furnace process, about one-half of the fluorine is tied up innocuously in residue or slag and discarded, but the remainder forms hydrofluoric acid or silicon tetrafluoride which are noxious gases. All plants must have

expensive installations to collect these gases, together with other dust and fume. Attempts to recover the fluorine have not been economic as the scrubber sludge is not sufficiently rich in fluorine to compete with commercial fluorspar.

A problem of long standing is to determine what can be done with the iron phosphide obtained in the electric-furnace production of phosphorus. In electric smelting all the iron in the furnace charge is reduced to iron phosphide which is tapped separately from the bottom taphole of the furnace. A small amount of iron phosphide is sold as an alloying agent, but most of its serves only to create a warehousing problem and lower the overall phosphorus recovery.

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PLATINUM-GROUP METALS

By Glen C. Ware [1]

THE METALS of the platinum group include platinum, palladium, iridium, osmium, rhodium, and ruthenium. Platinum is the most abundant and most important member of the group, but each has important industrial uses. All the platinum-group metals except palladium command prices much higher than that of gold.

Platinum-group metals are recovered principally as the chief product of some placers, as a byproduct of nickel-copper ores, and as the main product of platinum ores.

From the early 19th century until 1934 placers in the Ural Mountains in the U.S.S.R. produced most of the world supply of platinum-group metals. The Republic of South Africa and Canada led in production from 1934 until after World War II, when metal from Siberia allowed the U.S.S.R. to increase its estimated output to more than half that of the world.

World ore reserves will support consumption at the present rate for the foreseeable future. However, potential uses loom, which cannot be supplied under present conditions, and alternate materials must be found. Catalysts for fuel cells, for example, reasonably could demand many times the present output of platinum. Platinum-group metals are an essential part of our highly sophisticated industrial complex upon which our national security depends, quite apart from their specific military uses. They are among strategic and critical metals held in our stockpiles. United States production is insignificant; domestic consumption exceeds free world production and is likely to continue to do so in spite of expanding production in the Republic of South Africa. In the foreseeable future more than half of U.S. imports must be from the U.S.S.R.

BACKGROUND

In the 7th century B.C. an Egyptian artisan forged a single grain of platinum into a hieroglyphic character which he included with the silver characters used to decorate an etui, probably not distinguishing platinum from silver. Twenty-five centuries elapsed before the science of chemistry solved the riddle of the natural alloys of platinum and found ways to produce malleable metal suitable for the jeweler's art. Platinum found in placer sands along with gold was unavoidably recovered with the gold, and the artisan was obliged to separate the two metals because they fused readily to form hard alloys which he could not fashion into objects of art. Throughout the centuries, platinum grains were plucked one by one from the miner's pan, even into modern times. Indeed, gold placers have been abandoned because the work of separating the platinum was too costly.

The Spanish explorers in South America found platinum objects fashioned by Indian metal smiths who had developed techniques of soldering and alloying the refractory metal and of making from it articles of jewelry and objects of art. However, platinum had no value for the Spaniards because European artisans could not work it.

A firm basis for the chemistry of platinum was laid by an English doctor, William Lewis, who published in 1763 the first authoritative description of the metal and some of its alloys. He recognized the heterogeneous character of the crude platinum, but his most useful discovery was the use of ammonia to precipitate platinum from the solution obtained by treating crude platiniferous material with aqua regia. This practice remains in common use today. Meanwhile, Marggraf in Germany in 1757 had demonstrated the presence of iron in native platinum and had removed it, effecting the first recorded separation of the platinum-group metals from the crude mineral.

[1] Commodity specialist.

French workers, notably Macquer and Baumé unwittingly prepared platinum pure enough that it could be welded, forged, and rolled. Baumé noted that these properties and its noble character made it a desirable metal of commerce. Von Sickingen in Germany was able to draw wire 0.0113 of an inch in diameter, but he too did not realize that the secret of his success was iridium-free metal. Lavoisier in France contributed the oxyhydrogen flame which was hot enough to fuse the ammonia precipitates into massive metal.

In 1784, in Germany Achard fused platinum with arsenic and ground the brittle residue to a powder which he enclosed in a clay mold. The assembly was heated to drive off the arsenic, leaving a sintered shape of platinum. When this piece was forged cold on a mandrel, it became the first platinum cruicible. Daumy in France noted that fusion with arsenic refined the metal. Janety, in Paris, by 1787 had improved the process and expanded the scale to the point that massive metal was available for the arts and sciences.

Credit belongs to the English for the isolation of the separate platinum-group metals. Wollaston announced the discovery of palladium in 1803 and rhodium in 1804. Tennant isolated and named osmium and iridium in 1804. Claus, working at the University of Kazan, discovered ruthenium in 1844 and named the metal after his adopted country, Russia, but used the latinized name Ruthenia. During the 19th century, the last of the basic techniques for working platinum was developed when Hare, in 1801, melted platinum with a blowpipe and noted the refining effect of an oxidizing atmosphere upon the molten metal. Deville reduced melting to practice.

By the close of the 19th century platinum ware was in common use in laboratories. It had reached the scale of boilers to concentrate acids in commercial plants. An ingot weighing 100 kilograms had been cast. The catalytic properties of the metal had been applied to the oxidation of several elements and compounds, including the preparation of the anhydrides of sulfuric and nitric acids, the flameless oxidation of inflammable vapors, and the ignition of hydrogen in air. All of these and the catalytic application in oil refining were destined to replace the arts as the greatest users of platinum. Meanwhile changes were taking place in supply and marketing.

Russian metal had displaced that from Colombia, and Russia remained virtually the only source of platinum metals for nearly a century. A world trade had been established, centered in Paris, and the firms which now control the industry were beginning to emerge from the competing refineries in Europe.

Sales of platinum-group metals from Canadian nickel ore began about 1909, and in the early 1930's Canada became the world's chief source of these metals. The first metal from South Africa was marketed in 1925 and exports reached 60,000 ounces per year by 1941. It continued at this rate until 1950, when it began a sustained rise which is still in progress and is projected through 1965. South African production surpassed that of Canada from 1951 to 1957.

The U.S.S.R. does not report production or exports, but, based upon the amount of metal reaching world markets and the free world production, it is estimated that more than one-half of the world's platinum-group metals is produced in the Soviet Union.

All categories of use have increased, but unevenly. The application of platinum catalysts to petroleum refining brought a surge in the demand for platinum through the mid-1950's, and the application of palladium to electrical contacts in communication switch gear made a heavy demand on palladium throughout 1960–65. Presently, the need for refractory ware in which to melt laser compositions has increased the demand for iridium. These surges in demand are superposed upon the steadily increasing need to supply an economy which is growing in size and complexity.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

World output of platinum-group metals in 1963 was estimated at 2 million ounces, 66 percent of it produced by the U.S.S.R. Canada produced 16 percent, the Republic of South Africa 14 percent, and the rest of the world 4 percent.

U.S.S.R. production is believed to come chiefly from the Norilsk region of Siberia where the platinum minerals occur in basic and ultrabasic rock formations similar to the deposits of South Africa. The production from placer deposits in the Ural Mountains is of secondary importance, although platinum placers and platinum-bearing gold placers are found from the Urals to the Pacific (*4*).[2]

The Bushveld complex, a geological feature in the Republic of South Africa, is the source of nearly all of that nation's platinum-group metal output. The Rustenburg Platinum Mines,

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

Ltd., operates the mines and recovers a crude metal which averages about 70 percent platinum, 25 percent palladium, and 5 percent of combined iridium, osmium, rhodium, and ruthenium. The crude metal is refined by Johnson, Matthey & Co., Ltd., in England, which serves as importer, refiner and exporter. Through its affiliate, J. Bishop & Co. Platinum Works, Malvern, Pa., it fabricates and distributes the finished products. In 1964 a consortium of three mining companies led by Rand Mines contracted with the Rustenburg Platinum Mines, Ltd., to exploit the Brakspruit Mine, which adjoins the Rustenburg Mine at Rustenburg, and produce a crude concentrate. Engelhard Industries of Newark, N.J., will refine the crude and market refined metal and metal products. In the past Englehard has obtained all of its platinum-group metals from Canada. A small amount of osmiridium from gold ore reaches refiners outside England, including refiners in the United States.

The current expansion of production to full mill capacity, 675,000 ounces, is expected to be completed in late 1965, putting the Republic of South Africa in second rank. The amount and the grade of their reserve will permit further expansion if market conditions justify it.

Canadian production of platinum-group metals arises as a byproduct of the smelting of copper-nickel ores of the Sudbury district. When these ores are smelted the precious metals appear in the bessemer matte, and a crude precious-metal concentrate. They are recovered from the matte by chemical methods. The International Nickel Co. of Canada, Ltd., the chief producer, has a refinery in Acton, England, where the concentrate is refined and the metals are returned to Canada. Some are fabricated and some are exported to the United States. Englehard Industries, Inc., handles the refining and distributing of the metals in plants in Newark, N.J., and Toronto, Canada. Falconbridge Mines, Ltd., produces matte from Sudbury ore but ships it to Kristiansand, Norway, where platinum and palladium are recovered, and the remaining precious metal concentrate is returned.

The United States produced 50,000 ounces of platinum-group metals in 1963, 3 percent of the estimated world production. Output from Goodnews Bay, Alaska, is purchased by Johnson, Matthey & Co. and refined for them by its affiliated J. Bishop & Co. Platinum Works. Additional output comes from gold placers and from the refining of copper. Output from the latter source may increase with demand for copper, but output from placers is likely to remain static.

In addition to new supply of platinum-group metals, refiners reprocess scrap, worn equipment, spent catalysts, and other secondary material, returning to use an amount of metal virtually equal to the new supply.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

In world markets, platinum-group metals are measured in kilograms, but, where the English system of weights prevails, the troy ounce is used. A kilogram equals 32.15 troy ounces, and for comparison, equals 35.27 avoirdupois ounces. In the United States the troy ounce is used exclusively. The term fine ounce, referring to a troy ounce of contained metal, is seldom encountered.

Sponge is a term applied to an imperfectly consolidated chemical precipitate, the end product of chemical refining. Subsequent forging or melting is required to produce massive metal.

Rolled metal refers to metal such as silver or stainless steel which has been clad with a precious metal and rolled to reduce the thickness of the coat.

Normally the metals of the platinum-group are produced at a purity of more than 99.9 percent. However, platinum 99.999 percent pure is required for thermocouples and resistance thermometers. Chemically pure platinum contains less than 0.001 percent of impurities. Platinum 99.9+ percent pure is suitable for platinum utensils and electrical contacts, and, above 99.7 percent pure, it is graded commercial. A purity of better than 99.9 percent is required for the minor metals to be used as alloy constitutents.

According to Federal regulations an article of trade may be marked platinum if it contains 98.5 percent platinum-group metals with a minimum of 93.5 percent platinum. Special stamping provisions cover some of the alloys developed for the jewelry trade. Some States have stamping regulations in addition to Federal requirements.

TECHNOLOGY

Platinum-group metals occur in basic or ultrabasic eruptive rock. In basic rock they are usually too widely disseminated to be recovered profitably except as a byproduct of nickel and copper smelting. In ultrabasic rock, dunite for example, the crude alloys of platinum-group metals, often containing iron, are found as crystals or irregularly shaped solids where they are separated from the magma as the molten intrusion cools. Deposits of them are found in pipes, pockets, and lenses.

When weathering liberates the crude platinum, placer deposits are formed from which the heavier metal can be separated from the lighter rock by gravity. When the deposits are mined, these natural alloys are liberated by crushing and are separated by a suitable means such as with zinc amalgam, by flotation, or by tabling. When they occur in sulfide deposits they are smelted and appear in the matte of the other metals in the ore. In any case, the crude concentrate is refined chemically.

Platinum-group metals are not amenable to fire refining because of their high melting point and the lack of a parting method to separate the individual metals. Consequently, chemical methods are used to separate and refine them. But they are also resistant to chemical action, and aqua regia is needed for the initial attack. Methods vary, but in general they involve dissolving away the platinum, palladium, and gold with aqua regia, leaving a residue containing iridium, osmium, rhodium, and ruthenium. After the gold has been removed from the solution with ferrous sulfate, platinum chloride is precipitated with ammonium chloride. Palladium may be precipitated as a chloride by excess ammonia and hydrogen chloride. The chlorides of platinum and palladium separately are reduced to sponge metal which can be compacted and melted to massive metal. In analogous ways the undissolved residue from the aqua regia treatment can be put into solution; the metals iridium, osmium, rhodium, and ruthenium can be separated, reduced to metal, and fused to massive condition. Refining steps are needed for each metal before it is pure enough to use, generally more than 99.9 percent pure. Adaptations of these procedures are used; other methods may be employed, but those given here are typical.

Byproduct platinum-group metals from gold or copper ores are sometimes refined by electrolysis as well as by chemical means.

USES

Platinum finds its greatest use in the chemical industry where most of its special properties are exploited. In chemical ware it resists attack, in thermocouples it resists heat and oxidation, and in making nitric acid it is a catalyst which resists attack by the corrosive product. In spinnerets for spinning synthetic fibers it withstands both corrosion and erosion. Platinum's resistance to atmospheric corrosion is used in electrical heating elements and in pressure-rupture disks which would not respond reliably if atmospheric corrosion occurred. Delicate sensing instruments such as platinum resistance thermometers depend upon this same property for reliable performance.

Electrical uses make the second heaviest demand for platinum. It is wound into heating elements for furnaces and into resistance coils for precision instruments such as potentiometers. Where heat or mechanical conditions are more severe, iridium or ruthenium is alloyed with platinum to impart resistance to wear. Platinum is used as an inert anode material in electrodeposition and in cathodic protection of ships' hulls and other base metal fabrications. It is used for grids in high-power amplifier tubes, in reigniters for jet engines, and in platinum-mercury contacts in relays. A platinum-cobalt alloy containing 23.3 percent cobalt by weight is the most powerful magnet material known.

Pots for melting glass are made of platinum and its alloys, 10-percent rhodium being a common admixture for glass fiber manufacture. Platinum-rhodium alloy is used in pots to melt laser materials. Platinum cladding is satisfactory under less severe conditions.

Platinum and palladium are both used in the petroleum industry to catalyze the reforming of cracked petroleum fractions into high-octane gasoline. Both are used in jewelry to impart a brilliant luster. Palladium even exceeds platinum in amount used in dentistry and medicine.

The chief use of palladium, however, is in the field of communication where it is used largely to face electrical contacts in automatic switch gear, accounting for about 60 percent of its total use. Chemical use is second at 28 percent.

The minor metals, iridium, osmium, rhodium and ruthenium are used chiefly to harden platinum and palladium but electroplated rhodium is used in reflectors, electronic components, and in jewelry. Osmium and iridium are used to harden pen points and record-player needles. Radioactive iridium-192 is used in radiography.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Virtually all of the output of platinum-group metals produced is coproduct or byproduct in origin. Gold is always recovered with platinum-group metals from placers. Platinum-group minerals generally occur in ultrabasic or basic host rocks such as dunite and norite and are associated with other metal minerals, generally copper, nickel, or chromium. In Canada, copper and nickel are the main products, and presumably this is true in the U.S.S.R. In the Republic of South Africa, platinum-group minerals are the main product but are

associated more often with chromium than with nickel.

ALTERNATE MATERIALS

The high price of the platinum-group metals exposes their field of use to inroads by substitutes, and it restricts the expansion of their use. For example, in the field of catalysis, nickel boride and the oxides of nickel and cobalt compete for use in fuel cells. The life of the platinum reforming catalysts in petroleum refining is extended by treating the reformed distillate with a nickel catalyst. Vanadium is used in place of platinum in making sulfuric acid. The useful life of the platinum gauze catalyst used in the manufacture of nitric acid is extended by alloying it with rhodium.

Platinum is hardened with gold for use in spinnerets for the manufacture of rayon. There is considerable substitution within the group itself as well as alloying with metals of the group to increase hardness or strength. Nickel alloy wire is used for resistors instead of platinum wire where extreme stability is not required. Tungsten competes with platinum and palladium for use as electrical contacts where arcing occurs.

Cladding with platinum-group metals is a form of substitution where reliance is put on cheaper metals for mechanical strength and upon the noble metal for surface properties. This is common in glass melting pots and in other chemical ware. Rhenium is sometimes used where corrosion resistance is required.

SECONDARY SOURCES

The uses of platinum-group metals are generally not dissipative. An important exception is the use of palladium in electrical contacts. But, for the most part, outmoded jewelry, worn equipment, scrap, and sweeps can be processed to reclaim its platinum-metals content. Refined metal equal to more than 10 percent of the requirement for new metal is returned to domestic supply from such sources. Most of the spent catalysts and some of the material referred to above are refined on toll and returned to the user. The amount of metal returning to use through this channel is about the same as that of new supply.

RESERVES

The platinum-group metals reserves of Canada can be set at 12 million ounces from estimates based on reported reserves of nickel and their precious metal content. Canadian ore does not yield osmium. Not enough data are available to estimate the reserves of the rest of the world which accounts for 83 percent of current production.

In the absence of reported values the reserves were estimated from related information such as mineralization in host rocks which contain platinum-group metals, or, in the absence of this kind of information, from production itself, provided it was stable. Production from domestic placers is low and declining, hence, in the absence of proven measurements, U.S. reserves must be considered inconsequential. They may be about 50,000 ounces. Supply from domestic copper refining is not high, and it is more meaningfully given as projected production, since it cannot be exploited independently of copper.

Ultrabasic host rocks contain the bulk of the known reserves of platinum and related metals. In the Sudbury district of Canada the host rock is primarily norite and peridotite, and the platinum values are closely linked to nickel mineralization. Canadian reserves have been estimated at 12 million ounces, essentially the same value that would be derived from the published reserves of nickel-copper ore and its content of platinum-group metals (*1*). However, the reserves at Thompson are reputed to be adequate for 100 years, and certain operations at Sudbury are alleged to be projected beyond the end of the century. These values of reserves lead to an estimate of platinum-group metal reserves three times that based on reported ore reserves.

The platinum-group metal reserves in the Merensky Reef in the Republic of South Africa have been reported to be the world's largest known reserves, but the amount of metal is not stated nor are other reserves cited for comparison. Accordingly, these reserves must be estimated from projected production. Milling capacity in this area is known, and the periodic increases in it have been reported. By late 1964 it is projected to be 3.25 million tons of ore annually, yielding nearly 700,000 ounces of platinum-group metals (*6*). Prudent investment policy requires that minimum known reserves be a sizeable multiple of annual production, perhaps 10 to 20 times as much. On this basis the reserves in the Republic of South Africa are set at 7 to 14 million ounces. Of this reserve 12 to 24 percent may be palladium and 66 to 78 percent may be platinum. A proportion of 70 percent platinum, 25 percent palladium, and 5 percent minor metals is generally accepted. This estimate does not consider the reserve of osmiridium in gold ore.

Information about the nature and the amount of the reserves of U.S.S.R. is not available, but it is believed that the Ural placers are not rich

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or extensive enough to support that nation's estimated production, even when augmented with byproduct metal from nickel smelters. It is believed that the major part of that nation's output comes from Norilsk and from cupriferous pentlandites of the Kola peninsula.

The Norilsk copper-nickel sulfide ores are reported to have a low content of platinum-group metals, but some may contain as much as 10 ounces per ton. Since the composition of the Soviet Union's exports indicates that the palladium to platinum ratio is 60:40 it would seem that the palladium-poor output of the Urals is a minor contribution to the total, supporting the belief that the Norilsk region and the Kola peninsula are the major producing areas.

If one assumes that a mining industry would not be developed to the size of that in the U.S.S.R. unless at least a 10-year supply of ore were in sight, one may set U.S.S.R. reserves at a minimum of 10 million ounces of platinum-group metals. Apparent expansion of U.S.S.R. production points to a significantly higher figure for their reserves.

CONSERVATION PRACTICES

The high cost of platinum-group metals stimulates the adoption of ways to recover them from the residues from copper and nickel refining and from gold placers. Most of the production of these metals in North America is derived from these sources.

Platinum-group metals are reclaimed from used chemical ware, worn spinnerets, spent catalysts, and the like. The amount recovered is of the same order as that of new metal sold to consumers. The properties of these metals can be utilized by the expedient of coating or cladding other materials which furnish the desired form and mechanical strength. Alloying platinum and palladium with minor metals of the group increases their hardness and durability to a remarkable degree without appreciably affecting their noble properties. Even the catalytic properties of platinum are retained when it is strengthened with rhodium.

SOURCES OF STATISTICAL INFORMATION

In the United States, data on platinum-group metals including domestic mine production, recovery of refined metals from both new and secondary sources, sales to consuming industries by metals and uses, and dealer's stocks are gathered and compiled by the Bureau of Mines through canvassing of the industry. Data on imports and exports are supplied to the Bureau by the Department of Commerce. Statistical reports covering all these phases are issued by the Bureau quarterly and annually.

No foreign country reports its consumption of platinum-group metals. Canada reports production, but only for the group as a whole. Trade news items and company annual reports give enough information to estimate the production of the Republic of South Africa. Vague estimates of potential production in the U.S.S.R. can be projected from early geological reports; but at best, they can only help to make reasonable the estimates of actual production deduced from estimated world consumption and free world production. Colombian production is estimated from its exports to the United States.

TABLE 1.—*Annual averages for platinum-group metals, 1954–63*

[Troy ounces]

Domestic production from crude platinum and byproduct platinum metals	26,253
Domestic refining:	
New metals	58,732
Secondary metals	95,342
Imports of refined metals [1]	861,746
Domestic consumption as measured by sales:	
Platinum	352,937
Palladium	420,530
Iridium	6,702
Osmium, rhodium, ruthenium	28,820
Total	808,989
Exports (unmanufactured)	46,922
World production [2]	1,222,000
Stocks of refiners and dealers in the United States (Dec. 31, 1963)	699,575

[1] Includes acquisitions for stockpile.
[2] Revised figure.

TABLE 2.—*Domestic consumption of platinum-group metals by uses, in percent, 1949–58*

Use	Platinum	Palladium	Iridium, osmium, rhodium, and ruthenium
Chemical, petroleum and glass	60.0	11.9	44.6
Electrical	18.4	65.4	14.1
Dental and medical	4.6	10.4	1.4
Jewelry	15.7	11.0	25.9
Miscellaneous	1.3	1.3	14.0
Total	100.0	100.0	100.0

TABLE 3.—*Domestic consumption of platinum-group metals by uses, in percent, 1959–63*

Use	Platinum	Palladium	Iridium	Osmium, rhodium, ruthenium
Chemical	27.5	17.8	21.4	31.9
Petroleum	10.1	.9		.6
Glass	16.5		.3	22.2
Electrical	28.8	67.5	29.1	18.0
Dental and medical	5.3	8.8	4.0	2.6
Jewelry and decorative	10.3	4.0	42.7	18.8
Miscellaneous	1.5	1.0	2.5	5.9
Total	100.0	100.0	100.0	100.0

PRODUCTION, CONSUMPTION, AND TRADE

In 1963 the world consumed an estimated 2.5 million ounces of platinum-group metals. Reportedly the Republic of South Africa drew upon stocks for about 10 percent of its sales, and the U.S.S.R. also may have drawn upon stocks. After taking these withdrawals into account the estimated world production in 1963 was more than 2 million ounces, two-thirds of it coming from the U.S.S.R. The output of the U.S.S.R. is high in palladium and may account for as much as 80 percent of the world's production of palladium.

Production in the United States comes from placers in the Goodnews Bay district in Alaska, from gold placers in California, and from the refining of gold bullion and blister copper. Total U.S. production amounts to about 2.5 percent of the world total.

As of February 1964 unwrought platinum-group metals and ore continued to enter the United States duty free. Platinum-group metals in the form of unwrought alloys, however, are taxed 40 percent ad valorem. Rate of duty for gold-plated and silver-plated semifinished articles of platinum-group metals is 50 and 24 percent ad valorem, respectively. Statutory rates of duty for unwrought alloys of platinum-group metals and the gold and silver-plated semifinished articles are all 65 percent ad valorem.

STRATEGIC CONSIDERATIONS

The domestic new supply of platinum-group metals ranges from 3 to 5 percent of consumption, and there is little chance that output can be increased significantly. Only a relatively small amount of these metals is refined in the Western Hemisphere. Most of the free world refining capacity is in England and Norway. Consequently the supply lines are long, requiring up to 9 months for the metal in mined ore to reach market in refined condition. Of greater concern, however, is the fact that supply is inadequate. The free world does not produce enough platinum-group metals to supply U.S. industry. During 1958–63 the United States obtained an estimated average of 374,000 ounces of these metals per year from the output of the U.S.S.R. In 1963, the amount may have been more than 700,000 ounces. By merely withholding its platinum-group metals from the world market, the U.S.S.R. would not only cut off about one-half of U.S. new supply but would engender strenuous competition for the output of the free world.

In an emergency some metal could be diverted from nonessential uses, and the supply could be stretched by more expeditious processing of secondary metal. Since about as much secondary metal returns to use as comes through new supply, the potential may be of consequence. Curtailing exports could be only a minor factor. Dealers stocks tend to amount to about two-thirds of annual consumption.

GOVERNMENT PROGRAMS

Platinum-group metals have important defense applications. Owing to this fact and to a short domestic supply, their sales for nonessential uses were prohibited during World War II and the Korean war. In 1953, the Business and Defense Services Administration (BDSA), Department of Commerce established regulations giving top priority ratings to the platinum-group metals for defense purposes. These metals were also placed on the preferred list, which required a validated license for export to the Communist countries and to other countries that have no similar restrictions with Communist countries.

To enhance a possible domestic supply of platinum-group metals, prospectors are eligible for 50 percent financial assistance under a program administered by the Office of Mineral Exploration (OME), Department of the Interior.

On account of their strategic importance platinum, palladium, and iridium were specifically put on the Government's list of strategic materials. Although osmium, rhodium, and ruthenium were not on the list, they were periodically acquired by the Government. To assure the country a supply of platinum-group metals in the event of an emergency, the Government continually reappraises the needs of national security and revises the stockpile objectives accordingly. As of June 30, 1964, there was 13,937 troy ounces of iridium in the national (strategic) stockpile; 737,935 troy ounces of palladium, of which 89,811 ounces was in the national (strategic) stockpile and 648,124 in the supplemental stockpile; 766,309 troy ounces of platnium, of which 716,310 ounces was in the national (strategic) stockpile and 49,999 ounces was in the supplemental stockpile. An additional 33 troy ounces of platinum did not meet stockpile specifications.

Some disposals of the platinum-group metals were made during 1959–63. In September 1959 Congress approved the disposal of approximately 2,600 troy ounces of osmium, rhodium, and ruthenium. They were sold through sealed bids. Sales were carried by monthly quota at a rate designed not to disrupt the normal market. The disposal of these metals was com-

pleted during the first half of 1962. In addition, 7,884 troy ounces of palladium was sold during the second half of 1963.

PRICES

The prices of the platinum-group metals were essentially the same at the close of 1963 as they were in 1960. However, the prices of platinum and palladium declined during the year under the pressure of heavy offerings from the U.S.S.R., but regained their earlier levels when the pressure relaxed as a result of record imports by the United States and Japan. Near the end of 1963, trading in futures resumed on the New York Mercantile Exchange and January 1965 futures were traded as high as $102 per ounce.

During 1963, the price range per troy ounce for platinum declined from $80 to $85 to $75 to $80 and returned to $82 to $85 by yearend. The price range for palladium declined from $24 to $26 to $22 to $24 and then regained its previous level. Throughout the year the other metals of the group were quoted as follows: Iridium, $70 to $75; osmium, $60 to $70; rhodium, $137 to $140; and ruthenium, $55 to $60.

TAXES

Domestic platinum producers are granted a depletion allowance of 23 percent on income from domestic production and 15 percent on income from foreign production.

In addition to a 15-percent depletion allowance (of salable value of minerals), taxable incomes of operations outside the United States and within the Western Hemisphere are taxed at a rate of 34 percent, well below the U.S. corporate income tax rate of 48 percent.

Jewelry and other luxury items made of platinum-group metals are subject to 10-percent Federal excise tax on the sale price.

EMPLOYMENT

Employment in the platinum-group industry is highly diversified, ranging from top management, in both business and research, down through all levels of employment. It involves scientific talent and craft skills over a wide range of applications, including catalysts, manufacturing of jewelry, electroplating, chemical ware, and research.

Engelhard Industries, Inc., reported a total of 4,515 employees in 1963, but employee-years devoted specifically to platinum-group metals was not given. Figures from other refineries and from electroplaters and other employers are not available.

RESEARCH

Vigorous research is being pursued by industrial concerns on all phases of the technology of the platinum-group metals. The reports and patents which result are too numerous to cite, but certain fields of investigation are worthy of note.

Substantial effort is directed toward developing catalysts for fuel cells (*2*, *5*).

Homogeneous catalysis by platinum-group-metal salts attracted interest because it promises greater specificity than heterogeneous catalysis (*7*). Many applications of platinum-group metals to printed circuitry are under investigation (*2*, *8*). The classical applications to petroleum refining, hydrogen purification, resistance heating, catalytic oxidation, and to other uses have not been neglected by industrial research programs (*3*). A recent contribution was a cobalt-platinum alloy having the highest magnetic flux of any material known.

OUTLOOK

Worldwide use of platinum-group metals is increasing. This upward trend is expected to persist and become stronger as underdeveloped countries industrialize. In 1963, the United States consumed 37 percent more of these metals than were produced in the free world, and consumption will continue to increase; but by percent, other nations may increase faster. Japan's imports have risen rapidly recently owing to her industrial expansion.

Production in Canada is expected to increase at a moderate rate from the base set in 1963. The recent expansion in nickel capacity in Manitoba will treat ore with a lower precious metal content than the Sudbury ores, and it will not augment the supply of platinum-group metals as much as would a corresponding increase at Sudbury. A placer deposit is being developed in northern British Columbia. Estimates of its expected production are not available, but its immediate contribution will be minor.

Production in the Republic of South Africa is being expanded, and it should reach 675,000 ounces of platinum-group metals per year by late 1965. Further expansion is possible if the world market is favorable, but it would be at

a slower rate than the present one in which only the mining rate was increased to supply existing mills to full capacity.

Production in the U.S.S.R. is not known with certainty, but estimates of current output indicate that reserves have been adequate to support a large expansion in recent years, raising it to first place in world production. In addition to placers, the U.S.S.R. has platinum-bearing nickel ores similar to those in Canada, and it has platinum-group metal ores like those of the Republic of South Africa. It now appears that the U.S.S.R. has metal for internal development and will remain the chief supplier to the world markets.

The United States production is inconsequential in world supply and is more likely to contract than to expand. Reports from other sources of platinum-group metals, including Colombia, are too sparse to permit a useful prediction of production beyond the statement that only the three major producers will contribute significantly to world supply in the immediate future.

The categories of use will remain about the same as now and be subject to the same fluctuation as in the past. New uses cannot be ruled out, but the extremely high prices of platinum-group metals and the inflexibility of the supply of the minor metals discourages the development of new uses. For instance, should fuel cells attain successful application to power generation, their demand for platinum would exceed present world production. The four minor metals of the group are coproducts of and are held in rigid supply by the demand for platinum and palladium. New or expanded uses of them face the threat of price instability. The prices of platinum and palladium make them vulnerable to substitutes. Therefore, it is expected that except for periods of dislocation in supply, prices will remain stable for the present, but they may drift lower after South African production reaches full capacity.

PROBLEMS

The high price of platinum-group metals seems to be a secondary problem when considering their inherently unstable prices. Domestic production of these metals is negligible compared with consumption, leaving demand to be supplied by purchases on the open market. However, a great measure of stability is provided by the threat of substitutes in some of the larger categories of use. The major suppliers have met this threat by allocating metal to their regular customers at prices significantly below the highs reached on world markets, and price increases to these customers have been moderate. They have lagged behind the price movements in the world markets and in futures trading. This market policy has for a time, at least, successfully met the disruption caused when the U.S.S.R. virtually discontinued offerings of platinum-group metals on the world market during 1964 after glutting it in 1963. However, such a price control is not a reassuring substitute for a flexible supply in a free market.

The inflexibility of supply of the minor metals of the group hampers the development of techniques that use them. These metals are produced in smaller amounts as coproducts during the production of platinum and palladium which, in turn, are to a great extent byproducts or coproducts Although the amounts of the minor metal products and the proportion of the metals in them varies with the source, it seems not to be feasible to mine them selectively on a significant scale. Hence, the market for the minor metals is destined to remain thin, and prices capricious. The development of uses is further restricted because data covering the production and stocks of the minor metals are not available. New or expanded uses are not likely to be developed unless adequate supplies of the metals are assured.

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POTASSIUM

By Richard W. Lewis [1]

POTASSIUM is one of the triad of major elements necessary to sustain plant life. Although its chief use is as a fertilizer, there is a growing list of chemical uses for potassium compounds.

The largest deposits of potassium minerals occur in West Germany, East Germany, the U.S.S.R., and Canada; the major producing countries are the United States, West Germany, East Germany, France, and Spain. In the United States, the largest producing country in 1963, approximately 90 percent of production came from New Mexico; the remainder largely from California and Utah.

The need to eliminate dependence upon German imports, accented by the shortage during World War I, provided impetus to a search for potassium compounds by both Government and industry, which resulted in the discovery of commercial deposits in New Mexico in 1925. The Geological Survey and the Bureau of Mines participated in the search, and the Bureau of Mines engaged in beneficiation studies.

Although potassium compounds occur in many rocks and minerals, the commercial sources are limited to soluble salts in bedded salt deposits and brines. The major deposits of potassium compounds in the United States are part of the Permian salt basin that underlies parts of Colorado, Kansas, Oklahoma, Texas, and New Mexico, and the Paradox basin of southwestern Colorado and southeastern Utah.

Recovery from bedded deposits is by the room-and-pillar method and from brine reservoirs by pumping. Beneficiation includes ore dressing and fractional crystallization methods.

Resources in the United States are sufficient to meet the expected demand for more than 100 years. In addition, producers are developing huge deposits in Canada (*1*).[2]

Of the potassium compounds consumed in the United States, 94 percent is used by agriculture and the other 6 percent by the chemical industry in manufacturing diverse products, such as detergents, soap, glass, ceramics, textiles, dyes, and drugs. The consumption of potassium compounds largely follows that of fertilizers, for which there has been an ever-increasing demand. This trend is expected to continue.

There is no substitute for potassium compounds in agriculture; they are essential to maintain and expand food production.

Problems of the potash industry are concerned with economic means of utilizing the low-grade soluble and insoluble sources of potassium compounds.

BACKGROUND

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Before World War I, supplies and prices of potassium compounds were controlled by a German cartel and regulated by the German Government.

Realizing the need for a domestic supply of potassium compounds, Congress passed an act in 1911 providing funds to search for domestic sources and to perfect processes for extracting potassium compounds from materials of various types. The problem was originally assigned to the Bureau of Soils, U.S. Department of Agriculture, and the Geological Survey, U.S. Department of the Interior.

The blockade of Germany by Great Britain during World War I cut off imports and caused intensified efforts to produce potassium compounds domestically. By 1918, at least 128 plants were producing potassium compounds

[1] Commodity specialist.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

from kelp, wood ashes, lake brines, alunite, cement dust, beet sugar waste, blast furnace dust, and other sources. After the war foreign supplies again became available, and all but one domestic plant ceased operations.

Germany and France (which gained control of many former German potash mines as a result of the war) formed a syndicate to eliminate competition by dividing the U.S. market between them. New producing companies in Palestine, Poland, the U.S.S.R., and Spain gained admittance to the syndicate, and the sphere of operation expanded to include the world market. Owing to an antitrust suit by the United States, the syndicate closed its New York sales office in 1927 and established a Netherlands company to sell potassium compounds from the syndicate-member countries in the United States. This arrangement continued until the outbreak of World War II in 1939.

Meanwhile, a law was enacted in 1924 "authorizing investigation by the U.S. Geological Survey to determine location and extent of potash deposits in the United States." The law was amended to include the Bureau of Soils and later amended again to substitute the Bureau of Mines for the Bureau of Soils. The Geological Survey did the geological work and determined drill-hole sites, and the Bureau of Mines supervised the drilling. Under this authority, which covered the period 1926–31, 24 holes were drilled in Texas, New Mexico, and Utah, and cuttings were examined from oil wells throughout the United States. Salt beds, ranging from 1½ to more than 8 feet in thickness and containing 9 to 14 percent K_2O equivalent, were found in New Mexico and Texas.

The occurrence of potassium compounds in the Permian basin was widely publicized, and oil drillers in the region began to examine cuttings for salines. Oil well drillers east of Carlsbad, N. Mex., in 1925 encountered unusually thick beds of salines. Samples taken during drilling contained significant traces of potassium-bearing minerals. In 1926, the operating company put down a core drill hole close to the first drill hole and obtained a vertical cross section of the saline strata. The core revealed a substantial thickness of potassium-bearing minerals. Of major significance was the disclosure of a potentially commercial bed of sylvinite. Further exploration by Federal and private agencies revealed the presence, at a depth of approximately 1,000 feet, of a deposit of sylvinite equal in concentration of potassium chloride (KCl) and other essential characteristics to the better European deposits, and large enough to warrant development of mines and refineries.

A later exploration program by the Bureau of Mines blocked out a National Potash Reserve about 14 miles northeast of Carlsbad. This deposit was held by the Federal Government until 1957, when it was leased to a producing company.

On the basis of the earlier drilling, United States Borax & Chemical Corp. began mine development in 1929 and production in 1931. A second producer, Potash Co. of America, began development in 1933 and production in 1934. A third producer, International Minerals and Chemical Corp., began development in 1936 as Union Potash Co. and production in 1940.

Duval Sulphur & Potash Co., now Duval Corp. (beginning in 1951), Southwest Potash Corp. (1952), and National Potash Co. (1957), now operate mines and refineries in New Mexico. Kermac Potash Co., owned jointly by National Potash Co. and Kerr-McGee Oil Industries, Inc., was developing a mine near Carlsbad in 1964, expecting production in 1965. Annual capacity of the New Mexico field, the largest U.S. producing area, was about 2.9 million tons of K_2O equivalent in 1964.

The second most important producing area in the United States is southeastern California, where American Potash & Chemical Corp. recovers potassium salts and other industrial and agricultural chemicals from brine in the crystalline salt mass of Searles Lake (*3*). Operations began in 1916, and annual capacity of this plant was about 200,000 tons of K_2O in 1964.

These two areas supplied over 90 percent of all domestic production in 1963; the remainder came from Salduro Marsh, near Wendover, Utah (Bonneville, Ltd.); the wells of The Dow Chemical Co. at Midland, Mich.; and, as a byproduct, from cement plants in Maryland.

Texas Gulf Sulphur Co. started development of the first potash mine in Utah near Moab in 1961. The facility was completed and production was scheduled for early in 1965. Several other companies were exploring the potential of the Utah deposits, but no mines were in developing stages at the end of 1964.

Potash Co. of America began producing potash in Saskatchewan, Canada, in 1958 but operations were suspended in 1959 because of failure of the mine shaft. The shaft was repaired and the mine and facilities were ready for operation by the end of 1964. In 1957 International Minerals and Chemical Corp. began shaft sinking at its Esterhazy, Saskatchewan, property, and after considerable trouble and expense started producing in 1962. Kalium Corp. began production late in 1964, using

solution-mining methods on its deep deposits. By the end of 1964, two other companies, United States Borax & Chemical Corp., and Alwinsal Potash of Canada Ltd., had begun development operations, expecting production by 1968.

DEFINITION OF TERMS AND GRADES

The term "potash" was derived from pot ashes, which were originally obtained by evaporating, in iron pots, solutions leached from wood ashes. The present worldwide meaning of potash is twofold. When used as a noun it means K_2O equivalent, and when used as an adjective it means potassium compounds or potassium-bearing materials.

Sylvinite, the major ore from underground mines in New Mexico, Canada, and Europe, is a mixture of sylvite (KCl) and halite (NaCl).

Three potassium salts are produced in the United States for fertilizer use—chloride (muriate), sulfate, and potassium-magnesium sulfate. The chloride is produced in two grades—60 percent muriate and manure salts (20 to 22 percent K_2O). Potassium sulfate contains a minimum of 50 percent K_2O. The double sulfate contains 22 percent K_2O equivalent and 18 percent MgO.

Chemical-grade potassium chloride, containing less than 1 percent impurities, also is produced in the United States. This chloride is the basic material for producing many other potassium compounds used by the chemical industry.

The term "crop year," as referred to in this chapter, is the 12-month period ending June 30.

TECHNOLOGY

Geology

Potassium is found in rocks of many types and in the waters of lakes, rivers, and oceans. It has been estimated that 3.11 percent of the lithosphere is potash (K_2O equivalent). Sea water contains an average of 0.04 percent K_2O equivalent. Minerals generally classified as potash minerals are given in table 1. Carnallite, kainite, langbeinite, niter, and sylvite are soluble potassium-bearing minerals of current economic value. Alunite, glauconite, leucite, and polyhalite are considered potential mineral sources of potash. The other minerals listed are not likely to be of any commercial value, many being quite rare.

The principal deposits of soluble potassium salts occur in formations of Devonian age in Canada; of Permian age in the United States, the United Kingdom, central Europe, and the Urals; of Miocene age in Sicily and the Ukraine; and of Tertiary age in Spain.

The Permian salt basin in the United States underlies parts of Colorado, Kansas, Oklahoma, Texas, and New Mexico, but commercial beds of potassium minerals have been found only in New Mexico. Deposits in the Texas-New Mexico region are irregular in shape, thickness, and quality. On the basis of scattered drill holes, indications of deposits have been found over an area of approximately 3,000 square miles (*4*). Commercial operations have been limited to about 55 square miles east of Carlsbad, N. Mex. (*8*).

In the Carlsbad area the overburden comprises about 80 feet of sand, caliche, and gypsum. Underlying this cover is the Rustler formation, consisting of several hundred feet of gypsum, dolomite, and sand and gravel beds. Under this is the Salado salt formation, having a maximum thickness of 1,600 feet. The Salado formation comprises about 45 sulfate beds (gypsum, anhydrite, and polyhalite) and 45 halite beds. The potassium-rich horizons, approximately in the middle of the formation, are from 650 to nearly 2,000 feet beneath the surface and consist of numerous thin beds, chiefly sylvite mixed with halite, with some langbeinite and carnallite.

An extensive potash-bearing salt basin of growing importance, known as the Paradox basin, lies in southeast Utah and southwest Colorado. The potash deposits occur in the "saline facies" of the Paradox member of the Hermosa formation of the Pennsylvanian age. The saline facies consists of at least 29 evaporite cycles, 11 of which contain potentially valuable potash deposits. The area covers about 11,000 square miles, and nearly two-thirds is underlain by potash deposits ranging from 1,700 to 14,000 feet below the surface. The evaporite cycles were assigned numbers in a detailed study by R. J. Hite in 1960 (*7*). The most important of the deposits at the present time is salt bed 19, which was traced from Crescent Junction, Grand County, Utah, to northern Montezuma County, Colo., a distance of nearly 110 miles. Owing to extensive folding of the beds, potash at present is minable only in salt anticlines. Exploitation of the Cane Creek anticline deposit was begun by one company late in 1964. Several companies were exploring

TABLE 1.—*Potassium-bearing minerals*

Name	Composition	Potassium (K) content, percent [1]
Borates:		
Kaliborite	$KMg_2B_{11}O_{19}\cdot 9H_2O$	5.0–6.6
Rhodizite	$NaKL:Al_4Be_2B_{10}O_{27}$(?)	Variable
Carbonates:		
Buetschliite	$K_6Ca_2(CO_3)_5\cdot 6H_2O$	32.5 (t)
Fairchildite	$K_2Ca(CO_3)_2$	32.8 (t)
Kalicinite	$KHCO_3$	39.1 (t)
Chromates:		
Lopezite	$K_2(Cr_2O_7)$	26.6 (t)
Tarapacaite	$K_2(CrO_4)$	40.3 (t)
Halides:		
Avogadrite	$(K,Cs)BF_4$	Variable
Carnallite	$KMgCl_3\cdot 6H_2O$	14.1
Chlormanganokalite	K_4MnCl_6	36.4
Chlorocalcite	$KCaCl_3$	21.4
Douglasite	$K_2FeCl_4\cdot 2H_2O$(?)	
Elpasolite	K_2NaAlF_6	28.9
Erythrosiderite	$K_2FeCl_5\cdot H_2O$	12–24
Hieratite	K_2SiF_6	35.4
Kremersite	$(NH_4,K)_2FeCl_5\cdot H_2O$	12.1
Mitscherlichite	$K_2CuCl_4\cdot 2H_2O$	24.5 (t)
Pseudocotunnite	K_2PbCl_4	17.1
Rinneite	NaK_3FeCl_6	28.9
Sylvite	KCl	52.4
Nitrates: Niter (saltpeter).	KNO_3	38.6
Phosphates:		
Dehrnite	$(Ca,Na,K)_5(PO_4)_3(OH)$	1.0
Englishite	$K_2Ca_4Al_8(PO_4)_8(OH)_{10}\cdot 9H_2O$	4.5
Lehiite	$(Na,K)_2Ca_5Al_8(PO_4)_8(OH)_{12}\cdot 6H_2O$(?)	1.9
Leucophosphite	$K_2(Fe,Al)_7(PO_4)_4(OH)_{11}\cdot 6H_2O$.	6.6
Lewistonite	$(Ca,K,Na)_5(PO_4)_3(OH)$	4.9
Millisite	$(Na,K)CaAl_6(PO_4)_4(OH)_9\cdot 3H_2O$.	1.4
Minyulite	$KAl_2(PO_4)_2(OH)\cdot 3\frac{1}{2}H_2O$(?)	10.2
Taranakite	$K_2Al_6(PO_4)_6(OH)_2\cdot 18H_2O$(?)	6.6
Silicates:		
Apophyllite	$KCa_4(Si_4O_{10})_2F\cdot 8H_2O$	4.3 (t)
Feldspars:		
Anorthoclase	$K(AlSi_3O_8)$–$Na(AlSi_3O_8)$	2.0–5.8
Microcline	$K(AlSi_3O_8)$	14.0
Orthoclase	$K(AlSi_3O_8)$	14.0
Glauconite (greensand).	$K_2(Mg,Fe)_2Al_6(Si_4O_{10})_3(OH)_{12}$	1.9–7.1
Silicates—Continued		
Leucite	$K(AlSi_2O_6)$	17.8
Micas:		
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$	7.5
Lepidolite	$K_2Li_3Al_3(AlSi_3O_{10})_3(O,OH,F)_4$.	10.0 (t)
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	9.9 (t)
Phlogopite	$KMg_3(AlSi_3O_{10})(OH)_2$	9.4 (t)
Roscoelite	$K_2V_4(AlSi_3O_{10})(OH)_4$	6.9
Nepheline	$(Na,K)(AlSiO_4)$	.7–5.8
Sulfates:		
Alunite	$KAl_3(SO_4)_2(OH)_6$	8.7
Aphthitalite (glaserite).	$K_3Na(SO_4)_2$	19.7–35.3
Arcanite	K_2SO_4	44.9 (t)
Chlorothionite	$K_2Cu(SO_4)Cl_2$	26.3
Cyanochroite	$K_2Cu(SO_4)_2\cdot 6H_2O$	17.7
Euchlorin	K,Na,Cu basic sulfate	6.0–8.5
Hanskite	$Na_{23}K(SO_4)_9(CO_3)_2Cl$	2.4
Jarosite	$KFe_3(SO_4)_2(OH)_6$	7.6
Kainite	$KMg(SO_4)Cl\cdot 3H_2O$	11.0
Kalinite	$KAl(SO_4)_2\cdot 11H_2O$	8.6 (t)
Krausite	$KFe(SO_4)_2\cdot H_2O$	12.2
Krugite	$K_2Ca_2Mg(SO_4)_4\cdot 2H_2O$	13.0
Langbeinite	$K_2Mg_2(SO_4)_3$	18.8
Lecontite	$Na(NH_4,K)SO_4\cdot 2H_2O$	2.2
Leightonite	$K_2CaCu(SO_4)_4\cdot 2H_2O$	11.5
Leonite	$K_2Mg(SO_4)_2\cdot 4H_2O$	21.3
Manganolangbeinite	$K_2Mn_2(SO_4)_3$	16.4
Mercallite	$KHSO_4$	22.0
Metavoltine	$(K,Na,Fe)_6Fe_2(SO_4)_6(OH)_2\cdot 9H_2O$(?).	17.4
Misenite	$K_8H_6(SO_4)_7$	31.8
Palmierite	$(K,Na)_2Pb(SO_4)_2$	
Pieromerite (schoenite)	$K_2Mg(SO_4)_2\cdot 6H_2O$	19.4
Polyhalite	$K_2Ca_2Mg(SO_4)_4\cdot 2H_2O$	13.0
Potash alum	$KAl(SO_4)_2\cdot 12H_2O$	4.8
Syngenite	$K_2Ca(SO_4)_2\cdot H_2O$	23.9
Taylorite	$(K,NH_4)_2SO_4$(?)	36.0
Ungemachite	$Na_9K_3Fe(SO_4)_6(OH)_2\cdot 9H_2O$	9.6
Voltaite	$(K,Fe)_3Fe(SO_4)_3\cdot 4H_2O$(?)	3.7
Vanadium oxysalts: Carnotite.	$K_2(VO_3)_2(VO_4)_2\cdot 3H_2O$	8.6

[1] Best analysis available; otherwise theoretical, indicated by (t).

Sources: Palache, Charles, Harry Berman, and Clifford Frandel System of Mineralogy. John Wiley & Sons, Inc., New York, 7th ed., v. 1, 1944, 834 pp.; v. 2, 1951, 1124 pp.
Dana, J. D. Manual of Mineralogy. Revised by C. S. Hurlbut, Jr., John Wiley & Sons, Inc., New York, 17th ed., 1959, 609 pp.

the potash potential of other anticlines in the area.

The brine deposits of Searles Lake, Calif., and the Bonneville Salt Flats, Utah, resulted from the evaporation of large inland seas and contain various quantities of potassium in complex brines.

Mining

Potassium compounds are recovered in the United States from three types of deposits: The large salt beds of the Salado formation in New Mexico, the folded and faulted beds in the salt anticlines of the Paradox basin in Utah, and the brines of Searles Lake, Calif., and Bonneville Salt Flats, Utah.

In the bedded salt formations, the room-and-pillar method predominates, and recovery is about 60 percent. Subsequent pillar robbing, widely used throughout New Mexico, increases recovery to as much as 90 percent. All mines are highly mechanized, and both electric and diesel equipment is used (*6*, *14*). Undercutters and drilling jumbos prepare the mining face for blasting. Continuous-mining machines are used in some areas. Crawler-type loading machines load the broken ore into shuttle cars or onto belt conveyors for delivery to underground transfer points. From the transfer points the ore is hauled to the shaft by electric or diesel-driven trains or on belt conveyors. Belt haulage is rapidly replacing trains. One mine has a main belt line more than 7 miles long fed by shuttle cars and feeder belts; another has all belt conveyor haulage.

Primary crushing is done underground before hoisting. Skip loading and hoisting are automatic at most mines; the loading, hoisting, and dumping cycle usually is 2 minutes or less.

The mines in Eddy County, N. Mex., are about 1,000 feet deep. The National Potash Co. operation in Lea County, mines from a depth of approximately 1,800 feet. All mines produce from one level except that of International Minerals and Chemical Corp., which has workings on three levels. The ore in the

operating mines ranges from 4 to 14 feet in thickness and averages of 18 percent K_2O equivalent.

Room-and-pillar mining will be practiced by Texas Gulf Sulphur Co. at its new mine near Moab, Utah. The mine is highly mechanized, using continuous-mining machines and the usual undercutters, drills, and loaders. Ore haulage from ore body to the shaft, about 3,000 feet, will be by belt conveyor. As the mine development progresses, the main line conveyors will be extended and section conveyors added, with diesel shuttle cars transporting ore from the face to the conveyor.

Mining is expected to be on one level for several years, at a depth of about 2,800 feet. Primary crushing will be done underground before hoisting.

One circular shaft, 22 feet in diameter, is divided to provide for ventilation to the mine, an 80-man cage, and two 20-ton ore skips. A second shaft is to be added in the near future.

The recovery methods used at Searles Lake, Calif., described in the "Boron" and "Sodium and Sodium Compounds" chapters, exemplify methods of working brine deposits. About 3.7 million gallons of brine, containing about 2.5 percent K_2O equivalent, is pumped daily to the refinery from about 40 wells, 70 to 120 feet deep. Dissolved salts constitute over one-third of the weight of the brine.

Milling and Refining

Two basic methods of ore treatment—flotation and fractional crystallization—are used in the Carlsbad area to recover sylvite from the ore. Sylvite is separated from halite, the principal impurity in the ore, in a brine saturated with both sodium and potassium chlorides by either floating or depressing the sylvite. In general, sylvinite is mixed with the saturated brine and deslimed to remove most of the clay impurities. Then the flotation reagent, usually amine chloride or amine acetate, is added and the pulp is conditioned and sent to flotation cells where the sylvite is separated from the halite. The halite fraction is repulped and pumped to tailings, and the sylvite concentrate is dried and shipped or sent to storage.

Fractional crystallization is based on the relative solubilities of sodium chloride and potassium chloride in saturated solutions at changing temperatures. Crushed ore is mixed with the hot, saturated sodium chloride brine, which selectively dissolves the potassium chloride. The brine is then cooled, and the potassium chloride crystallizes as a 99-percent-pure product.

Langbeinite, produced in the United States by International Minerals and Chemical Corp., is separated from halite, its principal impurity, by selective solution of halite.

Potassium compounds are recovered from brines by evaporation and fractional crystallization. First, the sodium salts are separated in triple-effect evaporators, leaving a hot liquor rich in potash and borax. Rapid cooling under vacuum causes the potassium salts to crystallize. They are removed by settling and centrifuging.

USES

Potassium is one of the three major plant-nutrient elements, and approximately 94 percent of the potassium consumed in the United States is used in agriculture—usually in mixed fertilizers. The remaining 6 percent is consumed by the chemical industry.

Potassium chloride is the most widely used potassium compound in fertilizers; next in use are the sulfate and the double salt, potassium-magnesium sulfate. Several grades of potassium chloride (muriate) are utilized in fertilizers, standard, granular, and coarse, all containing a minimum of 60 percent K_2O equivalent, and run-of-mine or manure salts (20–22 percent K_2O). Some muriate with a 50 percent K_2O minimum is imported, but most of the foreign producers have raised the grade of their exports to that of the U.S. producers. Much of the potassium chloride, 62 percent K_2O and better, is used in the chemical industry.

Potassium sulfate contains 50 percent K_2O (minimum), and potassium-magnesium sulfate (sulfate of potassium magnesia) contains 20 percent K_2O and 18 percent MgO.

Crude potassium and crude potassium-sodium nitrate mixtures are imported from Chile for use as fertilizer materials. Potassium nitrate has been manufactured in very recent years for use as a fertilizer.

Of the potassium compounds used for agriculture, a small part is applied directly as a single-element fertilizer. The remainder is shipped to fertilizer factories, where it is blended with other plant foods to produce mixed fertilizers.

Metallic potassium has not been used commercially, because it costs more than sodium and is more difficult to handle. However, in recent research studies, the use of potassium vapor for driving reactor-powered turbines appeared promising. Small quantities of alloys containing potassium have special applications. Liquid mixtures of sodium and potassium have been used experimentally as coolants in atomic reactors, but the results were not encouraging.

Over 265,000 tons of chemical-grade potassium chloride was consumed in 1963; most was used to produce potassium hydroxide (caustic potash), the major chemical potassium compound. Most other potassium chemicals are made from potassium hydroxide. The major potash-chemical-consuming industries include detergents and soap, 35 percent; glass and ceramics, 25 percent; textiles and dyes, 20 percent; and chemicals and drugs, 13 percent.

Potassium hydroxide is used in manufacturing soaps and detergents, ceramics and glass, and textile dyes.

Potassium carbonate has diverse industrial and chemical uses. It is an ingredient of ceramics and glass, especially electrical glass. Potassium carbonate also is used in making textile dyes and in printing fabrics; in producing cocoa and chocolate, effervescent mineral waters, and special leavening agents; and in cleaning, treating, and electroplating metals.

More than 10,000 tons of potassium sulfate is used annually by the chemical industry. The major use (75 percent) is as an accelerator in manufacturing gypsum plasterboard and gypsum tile. About 6 percent of the industrial potassium sulfate is used in producing titanium pigments. About 1,400 tons, or 14 percent, is consumed annually in producing potash alums for water purification, fur treatment, leather tanning, pickle making, textile dyeing, and fireproofing and in manufacturing pigments, vegetable glue, artificial stones, porcelain cement, medicines, and photographic chemicals.

Potassium chlorates are used in making matches, explosives, propellants, and permanent-wave preparations. Potassium bromide is used chiefly in photography, photoengraving, and medicines. Potassium nitrate is used in manufacturing certain types of glass and ceramic glazes and in meat curing, pickling, and medicines. Potassium phosphates are used in detergents, penicillin processing, liquid soaps, and metal-plating baths. Potassium peroxydisulfate is a necessary ingredient in synthetic rubber manufacture. Potassium iodide is used in iodizing salt. Potassium bromate acts as an oxidizing agent in milling wheat flour.

There are many more chemical compounds containing potassium that have special research and industrial uses.

BYPROUCTS AND COPRODUCT RELATIONSHIPS

In the Carlsbad area, a small quantity of sodium chloride is sold as a byproduct of the potash industry for animal-feed supplements. Other byproducts include magnesium oxide and hydrochloric acid. Small quantities of cesium and rubidium are present in the Carlsbad potash ores, and other rare elements are associated with potash in this and other localities.

Potassium compounds recovered from brines are only one of many coproduct chemicals produced. For example, the principal products of the Searles Lake operations are soda ash, salt cake, potassium chloride, borax, bromine, and lithium carbonate.

Some potash is recovered as a byproduct in the manufacture of cement in Maryland.

The largest use of potassium compounds is as a source of potassium in mixed fertilizer containing phosphorus and nitrogen. Demand for and consumption of these three materials are closely related.

ALTERNATE MATERIALS

There is no substitute for potassium compounds in agriculture. They are not only necessary for plant growth but regulate the intake by plants of the other minerals and elements needed for normal plant growth. Some sodium compounds might be used in place of potassium compounds in certain chemical applications if the need arose.

RESERVES AND RESOURCES [3]

World resources of potassium compounds are sufficient for several thousand years at the present rate of consumption. The figures shown in table 2 are not necessarily comparable because the basis for measuring is not known for all countries. In general, the figures represent the total K_2O equivalent of the deposits.

The U.S. reserves are of two types, brines and bedded deposits. The brines of California, and Utah are estimated to contain approximately 120 million tons K_2O, while the bedded deposits of Utah and New Mexico have known reserves totaling about 340 million tons. The estimated reserves of potash in the United States follow:

	K_2O
	million tons
Brines:	
Great Salt Lake, known reserve	91
Great Salt Lake Desert including Wendover, Utah, inferred reserve	7.8
Searles Lake, Calif., known reserve	20
Michigan brine	Not available
Bedded deposits:	
Paradox basin (southeastern Utah and extending into southwestern Colorado):	
Known reserve	254
Inferred reserve	161
Permian basin (Carlsbad, N. Mex.):	
Known reserve	85
Inferred reserve	400

[3] Data for potash reserves in Utah and Colorado supplied by R. J. Hite, letter from U.S. Geological Survey. Other data for United States taken from "Potash Reserves of the United States," by Samuel H. Dolbear (American Potash Institute, Inc., Washington, D.C., 1946).

The estimate for the bedded deposits was based on a minimum bed thickness of 4 feet and a minimum equivalent K_2O content of 14 percent. A cutoff at 4,000 feet in depth was used in calculating the Paradox basin reserve. If solution mining of the deeper deposits of the Paradox basin was considered, the reserve figure for this area would be much larger.

TABLE 2.—*Estimated world reserves of soluble potassium compounds*

[Million short tons of equivalent K_2O]

Country	Quantity
Canada	17,500
France	350
Germany:	
East	10,000
West	9,500
Israel and Jordan (Dead Sea)	2,000
Spain	300
United States	450
U.S.S.R.	24,000

The Canadian reserve is based on an average equivalent K_2O content of 25 percent and bed thickness ranging from 5 to 10 feet. Because of unknown mining conditions in zones of multiple beds, only one bed was included in the estimate. The figure in the table for Canada is the total reserve. Assuming yields of 40 percent for mining and 90 percent for refining, the recoverable reserve would be 6.4 billion tons of K_2O.

Rich potash deposits with a combined reserve amounting to about 20 million tons have been discovered in Ethiopia and the Congo (Brazzaville).

Other possible sources of potassium compounds are alunite (*16*), carnallite, polyhalite (*4*), wyomingite (*16*), greensands (*15*), and porphyry-copper tailings (*11*). These sources, if commercial recovery methods were developed, would supply the United States for many hundreds of years.

Sea water contains about 0.04 percent equivalent K_2O, and each cubic mile contains the equivalent of 1.8 million tons of K_2O. Methods have been reported to recover 70 percent, but indicated costs are several times the 1963 selling price. Ultimately, however, the sea could provide a virtually unlimited supply of potash.

CONSERVATION PRACTICES

Improved mining practices have enabled recovery of up to 90 percent in the underground mines in New Mexico. Prior to the development of pillar robbing, mine recovery averaged 60 percent. Refinery recovery averages 90 percent of the contained K_2O equivalent.

A new flotation process, separating sylvite from langbeinite, was developed and put into operation during 1963. Langbeinite-sylvinite ores, previously uneconomical to mine and process, were made available, thus increasing the minable reserve.

SOURCES OF STATISTICAL INFORMATION

Data on crude ore production, marketable production and value, stocks, and total sales are collected semiannually by the Bureau of Mines, and 12-month data are published for years ending June 30 and December 31. Data on imports and exports of potassium compounds and production of certain potash compounds are collected by the Bureau of the Census, U.S. Department of Commerce. A canvass on consumption of potassium compounds in fertilizers, as measured by dealers' shipments, is conducted semiannually by the U.S. Department of Agriculture and published for years ending June 30. The American Potash Institute compiles and publishes quarterly data on potassium compounds deliveries (K_2O equivalent) in North America by destination. This statistical coverage is adequate for the needs of industry and government.

PRODUCTION, CONSUMPTION, AND TRADE

U.S. production, sales, imports, exports, and apparent consumption of potassium compounds are given in table 3. The marketable production of potassium salts (K_2O equivalent) in 1963 was 33 percent greater than in 1958. The only year not registering increased production during this 5-year period was 1962, when production dropped off 10 percent due to a 58-day labor strike in the potash mines of Carlsbad, N. Mex.

From 1959 through 1961, France, West Germany, and Spain were the leading countries from which potash was imported. In 1962, with the advent of Canadian potash production, Canada ranked third in U.S. imports; in 1963 it advanced to first place by contributing over 54 percent of the total.

Exports of potassium compounds rose 506,000 short tons K_2O equivalent in 1962 but dropped 16 percent in 1963.

All potassium compounds for fertilizer enter the United States duty free. The tariff on potassium chemicals ranges from 0.5 cent per pound for potassium hydroxide to 25 cents per pound for potassium iodide. On other potassium chemicals, not separately classified, the rate is 10.5 percent ad valorem.

The apparent consumption of potassium materials remained fairly level during 1959, 1960, and 1961 but started climbing in 1962 and in 1963 was over 25 percent greater than in 1958. This consumption amounted to about 30.5 pounds per year per capita.

Table 4 shows world production of potassium compounds in tons of K_2O equivalent.

TABLE 3.—*Salient potash statistics*

[Thousand short tons and thousand dollars]

	1954–58 (average)	1959	1960	1961	1962	1963
United States:						
Production of potassium salts (marketable)—quantity	3,599	4,033	4,472	4,629	4,167	4,867
Approximate equivalent K_2O quantity	2,120	2,383	2,638	2,732	2,452	2,865
Value [1]	$78,654	$80,393	$89,676	$104,464	$94,859	$109,276
Sales of potassium salts by producers quantity	3,565	4,191	4,412	4,226	4,615	4,588
Approximate equivalent K_2O quantity	2,100	2,476	2,602	2,487	2,722	2,713
Value at plant	$77,794	$83,903	$88,417	$95,388	$105,608	$103,152
Average value per ton	$21.82	$20.02	$20.04	$22.57	$22.89	$22.48
Imports for consumption of potash materials—quantity	319	432	415	465	617	1,041
Approximate equivalent K_2O quantity	172	234	226	262	341	594
Value	$11,374	$15,737	$15,370	$17,315	$21,765	$31,137
Exports of potash materials—quantity	344	572	833	803	859	722
Approximate equivalent K_2O quantity	182	337	491	473	506	425
Value	$13,077	$18,496	$25,926	$32,477	[2] $30,731	$25,519
Apparent consumption of potassium salts [2]—quantity	3,540	4,051	3,994	3,888	4,373	4,907
Approximate equivalent K_2O quantity	2,090	2,373	2,337	2,276	2,557	2,882
World: Production (marketable):						
Approximate equivalent K_2O—do	8,300	9,400	10,000	10,700	10,800	12,000

[1] Derived from reported value of "Sold or used."

[2] Measured by sold or used plus imports minus exports.

TABLE 4.—*World production of marketable potassium compounds, by major producers*

[Thousand short tons of K_2O equivalent]

Countries	1954–58 (average)	1959	1960	1961	1962	1963
Canada		47			150	600
France	1,428	1,611	1,689	1,885	1,898	1,900
Germany:						
East [1]	1,605	1,764	1,836	1,846	1,930	1,984
West	1,845	2,023	2,181	2,253	2,139	2,115
Spain	253	270	291	289	259	275
United States	2,120	2,383	2,639	2,733	2,453	2,866
U.S.S.R. [1]	918	1,160	1,216	1,455	1,650	1,875
Total [2]	8,300	9,400	10,000	10,700	10,800	12,000

[1] Estimate.

[2] Partly estimated and rounded. Includes minor producing countries.

STRATEGIC CONSIDERATIONS

Although import tonnage totaled nearly 21 percent of domestic consumption in 1963 and annual increases are expected from Canada, the United States is more than self-sufficient in potassium.

Potassium compounds are not on the Government list of strategic and critical materials even though they are essential for maintaining and expanding the agricultural output of the United States. Domestic production has been concentrated in southeastern New Mexico and is likely to remain so for several years. In addition, southeastern Utah is expected to become a major producing area within the next 5 years.

GOVERNMENT PROGRAMS

The potassium-bearing lands of New Mexico are owned largely either by the State or Federal Government and are leased from them by the individual firms. The brine deposits in California and Utah are partly Federally owned. Under an act of Congress approved February 7, 1927, entitled "An Act To Promote the Mining of Potash on the Public Domain" (44 Stat. 1057, 30 U.S.C. 281), the Secretary of the Interior is authoried to issue prospecting permits for a period not to exceed 2 years, sub-

ject to such rules and regulations as he may prescribe. The Code of Federal Regulations, Title 43—Public Lands, Interior, Part 194, Potassium Permits and Leases, governs exploration, development, and production on the public domain. Rental for Federal land is 25 cents per acre for the first year, 50 cents per acre for the second through the fifth years, and $1 per acre for each subsequent year. Rental is credited toward any royalties due. After a "startup" period of reduced royalty, all producers pay a 5-percent royalty on gross value of potassium compounds and related products.

As almost all the major producing areas in the United States are on the public domain, the rules and regulations under which the Secretary of the Interior issues permits have a vital effect upon the industry.

In addition to these controls, the Geological Survey supervises potash operations on the public domain under terms of the lease.

PRICES

Prices for potassium compounds are quoted on the short-ton unit (1 percent, or 20 pounds, K_2O per ton) and f.o.b. the mine. Bulk prices for New Mexico muriate, 60 percent K_2O minimum, in the crop year 1963–64, depending upon the order and delivery dates, ranged from 35 to 40 cents per unit for standard grade, 36 to 41.5 cents for coarse, and 37 to 44 cents for granular. Sulfate of potash, 50 percent K_2O minimum, ranged from 67 to 76 cents per unit, and manure salts (run-of-mine) remained steady at 17.65 cents.

TAXES

No special Federal taxes are imposed on the potassium-compounds industry. Producers in New Mexico are subject to a severance tax of 2.5 percent of the gross value of sales. Producers are granted a depletion allowance of 15 percent on both domestic and foreign production.

TRANSPORTATION

Potash ores are usually processed in refineries adjacent to the mines, and the marketable product is shipped by rail to the consuming areas. Table 5 gives the February 1964 freight rates for domestic shipments to selected cities from Carlsbad, N. Mex., Trona, Calif., Wendover and Potash, Utah, and Yarbo, Saskatchewan, Canada. Shipments for export are given a lower freight rate to the port of embarkation. In the major consuming areas, mainly east of the Mississippi, transportation costs amount to about one-half the price of the muriate. The eight States bordering the Great Lakes account for more than 40 percent of the total U.S. consumption. Canadian potash has a slight freight advantage over potash from Carlsbad in much of this area and is competitive in the rest.

Freight advantage for imported potash from Europe extends inland 100 to 150 miles from the Atlantic seaboard ports of entry.

TABLE 5.—*Freight rates per short ton for muriate of potash (including manure salts) and sulfate of potash from the major producing centers for domestic shipments, minimum weight 80,000 pounds, February 1964*

Destination	From Carlsbad, N. Mex.	From Trona, Calif.	From Wendover, Utah	From Potash, Utah	From Yarbo, Saskatchewan
Atlanta, Ga	$16.49	$18.67		$17.14	
Baltimore, Md	18.13	19.98		18.13	
Boston, Mass	18.67	20.53		18.67	
Buffalo, N.Y	17.15	19.33		17.15	$17.15
Chicago, Ill	15.08	17.26	$15.62	15.08	15.08
Cleveland, Ohio	16.49	18.67		16.49	16.49
Denver, Colo	13.67	16.20	13.67	6.66	
Detroit, Mich	16.49	18.67		16.49	16.49
Fargo, N. Dak	13.67	16.20	13.67	13.67	12.72
Indianapolis, Ind	16.28	18.46		16.28	16.28
Jacksonville, Fla	17.04	19.76		17.69	
Los Angeles, Calif	15.25	6.30	15.20		
Minneapolis, Minn	13.67	16.20	13.47	13.67	12.92
Montgomery, Ala	15.51	18.46		16.16	
Montreal, Quebec	19.38	21.45			15.07
Omaha, Nebr	13.27	15.80		13.27	13.77
Phoenix, Ariz	14.05	13.25			
Pocatello, Idaho	18.70	16.15	10.55	14.65	
Portland, Oreg	17.15	14.65	14.65	14.65	17.15
St. Louis, Mo	13.67	16.20		13.67	15.77
Salt Lake City, Utah	17.15	14.65			
Seattle, Wash	17.75	15.25	15.05	15.25	17.75
Sioux City, Iowa	13.27	15.83		13.27	13.27
Texarkana, Tex	10.70	16.20		15.28	
Toronto, Ontario	17.65	20.65		20.74	15.07
Vancouver, British Columbia	20.15	17.65	17.65		17.00
Wichita, Kans	13.27	15.80		13.27	

RESEARCH

As a result of the shortage of potassium compounds during World War I, Government agencies, private research organizations, and individuals investigated all the then known sources. In an attempt to increase the supply in the United States, the Bureau of Mines devised methods of recovering potassium salts from alunite, wyomingite, polyhalite, greensands, and porphyry-copper tailings. The methods were not perfected, because the indicated cost was excessive, domestic deposits of soluble ores were discovered, and imports again became available. As a result of research, participated in by the Bureau of Mines in the early 1930's, to devise ore dressing techniques adaptable to soluble salts, flotation is now used extensively in the New Mexico potash field.

Dry beneficiation techniques to separate sylvite from halite ore have been sought; however, experiments with laboratory-scale equipment were only partly successful. Fines and

small quantities of sulfate minerals caused incomplete separation.

Fertilizer research by the U.S. Department of Agriculture includes projects on producing and using high-analysis potassium-bearing fertilizers.

The American Potash Institute research program, active for more than 25 years in North America, deals largely with correct fertilizer usage.

Attempts have been made in the United States, Canada, and England to recover soluble potassium compounds from underground deposits by solution mining. Until recently none of these attempts have been successful. Late in 1964, however, a solution method was used for commercial production in Saskatchewan, Canada. Several other firms in the area are studying the technology and economics of using the solution technique on their properties.

OUTLOOK

Potassium mineral resources are adequate to meet any forseeable future demand. Present capacity is capable of meeting the short-term demand. Expansion of operating properties and development of new deposits are expected which should make it possible to supply the anticipated world demand of 20 million tons K_2O by 1980.

Further development of Canadian deposits will enable production of over 3 million tons of K_2O equivalent by 1970. Canadian material will continue to compete with domestic material in the major consuming areas of the United States. In addition, Canadian potash will be a strong competitor of domestic potash for foreign markets.

No new agricultural uses for potassium compounds are foreseen; however, demand for higher analysis materials will continue to increase. The agricultural need also will expand. With years of growing crops which use somewhat more potassium than is added annually as fertilizer, the soil becomes more and more deficient in this important plant nutrient. It thus becomes necessary to add as much potassium to the soil as the amount removed by the crops. An estimated 5 million tons, K_2O equivalent, are removed annually by cropping.

Discovery of deposits nearer the major consumer areas would encourage increased utilization. New industrial uses of potassium compounds will be developed, such as new explosives and propellents, but the requirements probably will not be large compared with total consumption of potassium compounds.

Although the reserves are enormous, insoluble potassium-bearing minerals will not contribute materially to the world supply in the foreseeable future.

PROBLEMS

The removal of potassium compounds from the soil by crops, solution, and erosion presents an obstacle to providing agricultural products needed for a continually rising standard of living for an increasing population.

Increased competition from imports, especially from Canada and Europe, hinders expansion of the domestic producing industry.

Technologic problems are the lack of economic mining and beneficiating techniques for recovering potassium compounds from lower grade sylvinite and polyhalite beds, such as those that could be exploited from present mine workings in New Mexico.

A long-range problem—to insure complete self-sufficiency for the United States virtually forever—is to find ways of utilizing the potassium compounds found in insoluble minerals and in saline water.

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PUMICE

By Timothy C. May [1]

ONE of the products of volcanic action is a sponge like cellular rock, pumice, which floats on water and is exceptionally resistant to both chemical and physical destruction. Its unusual characteristics have made pumice a useful construction material and abrasive throughout man's history.

In the United States pumice in consolidated form was used for building construction in California as early as 1851. From that date through 1963 the domestic pumice industry has grown to 2.6 million short tons of annual domestic output, valued at $6.6 million, produced from 103 operations in 15 States. Arizona is the leading domestic source, and Italy and Greece are the major foreign sources.

Of all domestic pumice and pumiceous materials used in 1963, the principal uses were 34 percent as aggregate and concrete mixtures, 32 percent for road construction, and 23 percent as railroad ballast.

Pumice deposits have been formed from lava flows and particles ejected explosively from volcanoes and transported and classified by air currents. Commercial pumicite deposits range from Tertiary to Recent, and older rocks formed from pyroclastic materials occur in strata as old as Ordovician.

Mining is usually open pit, and the overburden and pumice are removed by standard earth-moving equipment. Processing includes crushing, screening, and sometimes drying. For producing abrasive grades, grinding and air separation are usually employed.

Pumice resources are ample, but many deposits are in remote areas.

The problems of industry include the high cost of transportation to markets, health hazards, nuisance difficulties caused by dust, lack of sufficient research on mining, processing, and marketing, and stockpiling of excessive quantities to meet various size requirements of consumers.

BACKGROUND

As early as 1851 buildings in California were constructed of rhyolite tuff, a rock composed of consolidated pumice fragments. Probably the earliest record of domestic pumice production for abrasive purposes was in 1883, when 70 tons was mined from a deposit at Lake Merced near San Francisco. Ground pumice was mixed with cement and used as lining for the Los Angeles Aqueduct, constructed from 1908 to 1918 (*4*).[2]

Notwithstanding the early use of pumice in the domestic construction industry, the United States lagged behind other countries in recognizing the utility of pumice in the lightweight aggregate field. Before World War II Germany had built up a substantial export trade in lightweight building-construction units. However, the large-scale use of pumice as concrete aggregate in the United States did begin in 1935 and has increased rapidly since then.

Vesuvius has been the source of much of the Italian pozzolan cement, so named from the town of Pozzuoli near Naples. Cement containing volcanic debris was used in constructing parts of the famous Roman walls, aqueducts, the old Roman harbor works at Porto Trejano, Porto d'Anzio, and in other historic structures. These have proved the lasting qualities of pozzolanic cements.

SIZE ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

In 1963, 97 companies, individuals, or local government agencies operated 103 mines pro-

[1] Commodity specialist.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

ducing pumice or pumiceous materials. Those handling the largest tonnages shipped relatively low-value products used for railroad ballast, road construction, and lightweight aggregate. In 1963 the total domestic production, including scoria and related material, was 2.6 million short tons valued at $6.6 million at the mines.

Pumice or other detrital volcanic material is widely distributed. Commercial production in 1963 was confined to deposits of relatively recent geologic age in 14 Western States and Hawaii. These producing States were Arizona, California, Colorado, Idaho, Kansas, Nebraska, Nevada, New Mexico, Oklahoma, Oregon, Texas, Utah, Washington, and Wyoming. Deposits of pumice and pumicite have been mined in Alaska (*12*).

Important foreign sources include the Lipari Islands off the northern coast of Sicily, Santorin Island of the Greek Archipelago, the Rhine Valley, Germany, Austria, Japan, and southern France. Canada has unworked deposits in Saskatchewan and British Columbia.

Although volcanic explosions of past geologic periods have distributed volcanic ash and dust over a large part of the world's surface, only the more geologically recent eruptive areas now provide commercial pumice deposits.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Pumice is a highly cellular, glassy lava, acid to basic in chemical composition and essentially unaltered since formation. Much of it will float on water. The vesicles in pumice were formed by expanding water vapor and possibly other gases while the lava was in a plastic condition. Most pumice is white to gray, although other constituents sometimes impart a red, yellow, brown, or black color. The dark-colored pumiceous materials are formed from basic magmas and usually called *volcanic cinder*, *cinder*, or *scoria*. Other terms frequently applied to pumiceous or scoriaceous materials are *lapilli*, *black ash*, *volcanic ash*, or *volcanic dust* (*13*). All these terms are applied loosely and have not been defined by way of chemical composition other than that the light-colored materials are trachytic or acidic and those of dark color are basic.

Pumicite denotes concentrated sand-size particles of natural volcanic glass ejected from volcanoes during periods of eruption and subsequently more or less classified while transported by winds. The particles may be wholly unconsolidated or somewhat cemented. In the latter instance the resulting rock is usually defined as a *tuff*. *Welded tuffs* are the result of the cementation of pumice particles caused by volcanic heat. *Trass* is a German term applied to a light-colored, silicified, trachytic tuff occurring especially in the lower Rhine valley.

In addition to pumice, in commercial parlance a concentration of detrital volcanic material such as pumicite, volcanic cinder, volcanic ash, and scoria is frequently grouped as pumice. Except where specifically qualified in this chapter, the term will be used in the inclusive commercial sense.

An average chemical analysis of eight domestic and foreign pumice samples, in percent, is: SiO_2, 70.86; Al_2O_3, 1.41; Fe_2O_3, 1.33; FeO, 2.05; MgO, .74; CaO, 1.72; Na_2O, 3.60; K_2O, 3.28; H_2O, 2.88.

Standard screen sizes of ground pumice offered by the trade ordinarily range from minus 6-mesh for use in tumbling barrels or coarse metal finishing to minus 200-mesh for fine polishing. Finer particle sizes are obtained by air floating in air cyclones and other forms of air separation. These fine sizes are used for special cleaning and polishing compounds, principally in the glass industry.

Pumice for abrasive use should be extremely vesicular, with vesicle walls thin but strong. It should be uniform in composition, free from oversize particles or particles harder than the homogeneous pumiceous mass. Flat, platey grains are undesirable; the ideal shape would be cubic. It is customary for most grades to be selected on an experience basis owing to the difficulty of anticipating the performance of pumice of various grain sizes and sources on specific materials under various abrasive operating conditions.

Specifications of pumice used for railroad ballast, road surfacing, and aggregate are much less stringent than for abrasive use. Such material is often used with little preparation and sells at a relatively low price.

Pumice, while in itself possesses no cementitious value, will in finely divided form and in the presence of moisture chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties (*8*).

The actual specific gravity of pumice is about 2.5. The bulk density, of course, varies with the percentage of voids present. Fine material from Deming, N. Mex., after crushing, weighs 1,200 to 1,300 pounds a cubic yard, and the coarse weighs 800 to 900 pounds a cubic yard. The moisture content of this pumice varies from 5 to 20 percent, depending on the season.

TECHNOLOGY

Geology

Pumice and associated materials are products of explosive volcanism, and commercial deposits usually are found as concentrations near active or geologically recent volcanoes. Many pumicite deposits are composed of pumiceous particles transported many miles by air currents; other deposits are found on the flanks of volcanic cones.

This transported material extends to the Eastern States forming impure, noncommercial, pumiceous accumulations. Many have been consolildated into beds, which are only slightly altered. Frequently earlier beds have undergone severe metamorphism. The geologic age of most domestic, commercial pumice and pumicite deposits ranges from Tertiary to Recent (*11*).

The light colored pumice and volcanic ash are acidic to subacidic in chemical composition, whereas volcanic cinder, scoria, and dark pumiceous materials are much more basic. On the basis of mode of deposition, size distribution of the particles or fragments, and origin of the material, deposits of pumice and pumicite have been grouped into a number of types (*7*) : (1) subaerial deposits, (2) subaqueous deposits, (3) vesiculated surfaces of obsidian domes or flows, (4) reworked deposits, and (5) "nuée ardente" deposits—deposits formed by a swiftly moving, often violent horizontal ejection of gas-charged, highly heated viscous lava, carrying large and small lava fragments and accompanied by a cloud of gas and ash.

Mining

Although some pumice mining in California has been underground, almost all current production is from open pits.

Overburden usually is present and is removed by standard methods. Well-consolidated tuffs sometimes must be blasted. Loose pumice particles and loosely consolidated tuffs generally can be excavated with a bulldozer or dragline.

The bulldozer can move the material to storage piles near loading chutes or directly over tunnels enclosing belt conveyors for delivery to trucks or screening plants.

Milling

A scalping screen usually removes vegetable matter and oversize lumps. Rolls and hammer mills may be used to reduce oversize fractions; various screening and blending systems are used to produce the desired gradings.

Pumice may be dried in rotary driers either before or after crushing. The finer sized products, for abrasives, are produced with air separators and screens. Some pumice has been beneficiated on pneumatic concentrating tables.

Pumice products for abrasive use are packed in paper or burlap bags or barrels for shipment. Aggregates are shipped in bulk.

Domestic pumice is prepared for market near the mine; foreign pumice usually is imported in the crude state. Imported abrasive grades are crushed, ground, dried, screened, and air separated at plants on the eastern seaboard. Foreign crude pumice requires little preparation for use as a lightweight aggregate.

USES

Until the mid-1930's the only important domestic use for pumice was as an abrasive. Thereafter, its use developed as a lightweight aggregate for concrete and with gypsum in acoustic fire-retardant building plaster. The use of volcanic cinder and scoria for road surfacing and railroad ballast has become a major use for this material. Pumice is also becoming important as a pozzolan in hydraulic cements (*1*). Ground pumice and volcanic ash, added to hydraulic cements, improve workability of the concrete, counteract excessive free lime, increase strength, and improve durability (*4*).

Smaller quantities are used for many purposes including cleansing and scouring compounds and hand soaps, other abrasive uses, diluents, absorbents, and carriers for insecticides, herbicides and fungicides, filter beds,

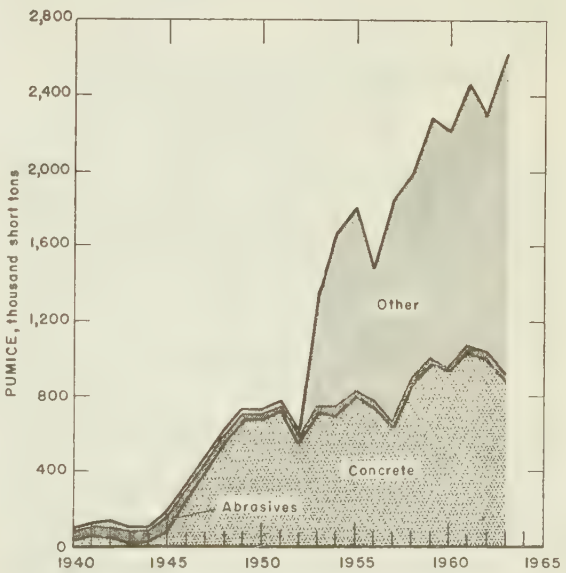

FIGURE 1.—Trends in Pumice by Uses.

lightweight refractory brick, soil conditioning, catalyst carrier, decolorizing and purifying agents, packing, filler and extenders for paints, enamels, varnishes, plastics, paper and rubber goods.

ALTERNATE MATERIALS

Under various conditions pumice competes as a lightweight aggregate with expanded clays and shales, expanded perlite, exfoliated vermiculite, slag, cinders, and diatomite. Expanded perlite and foamed glass are virtually synthetic pumices (*10*).

As an abrasive in block form, pumice competes in the market with brick made from silicon carbide, aluminum oxide, and natural rock such as novaculite and sandstone.

In the form of loose abrasive grain, pumice and pumicite encounter competition from garnet, silica sand, tripoli, diatomite, aluminum oxide, and silicon carbide.

Among the substitutes for pumice and pumicite used as pozzolans are fly ash and diatomite.

Exfoliated vermiculite and expanded perlite compete with pumice in the acoustic plaster market.

RESERVES

Domestic resources occur principally in Arizona, California, Hawaii, and Oregon. They are very large and appear adequate to meet foreseeable demands.

Foreign localities where major pumice resources occur are France, West Germany, Greece, Italy, and New Zealand. These deposits should provide ample quantities for importation into the United States. Recent exploration reveals substantial deposits in the lesser Antilles Islands.

SOURCES OF STATISTICAL INFORMATION

The Bureau of Mines canvasses all known pumice operators annually. Most pumice miners are comparatively small-scale producers and many operate intermittently. Thus only a minimum of statistical detail has been accumulated.

PRODUCTION, CONSUMPTION, AND TRADE

Domestic pumice sold or used by producers in the United States is shown in table 1.

Fourteen States west of the Mississippi and Hawaii produced pumice or pumiceous materials in 1963. Arizona with 10 active mines was the largest producer. California with 33 mines was next as shown in table 2.

TABLE 1.—*Pumice sold or used by producers in the United States*

[Thousand short tons and thousand dollars]

Year	Pumice and pumicite		Volcanic cinder		Total	
	Quantity	Value	Quantity	Value	Quantity	Value
1954–58 (average)	933	$2,869	813	$1,332	1,746	$4,201
1959	784	3,267	1,492	2,596	2,276	5,863
1960	601	2,767	1,609	2,802	2,210	5,569
1961	936	4,203	1,527	2,596	2,463	6,799
1962	533	3,206	1,738	3,095	2,271	6,301
1963	1,050	3,321	1,568	3,257	2,618	6,578

During 1963, 34 percent of all pumice consumed was used as aggregate and concrete mixtures, 32 percent for road construction, and 23 percent as railroad ballast.

TABLE 2.—*Pumice sold or used by producers in the United States*

[Thousand short tons and thousand dollars]

State	1962		1963	
	Quantity	Value	Quantity	Value
Arizona	756	$1,640	800	$1,877
California	573	2,615	460	2,017
Colorado	76	82	60	87
Hawaii	232	380	274	469
Idaho	67	103	161	275
New Mexico	308	741	322	850
Oregon	(1)	(1)	422	664
Utah	28	46	28	46
Wyoming	42	41	(1)	(1)
Other States [2]	189	653	91	293
Total	2,271	6,301	2,618	6,578
American Samoa	50	108		

[1] Figure withheld to avoid disclosing individual company confidential data; included with "Other States."
[2] Kansas, Nebraska, Nevada, Oklahoma, Texas, and Washington.

Pumice used as a concrete aggregate, railroad ballast, and for road surfacing is sold in a low-price market and must compete with many substitutes. Hence the market area for any deposit is limited by transportation costs and the availability of competitive materials. As abrasives, pumice sells at a much higher average unit price; transportation is a smaller part of the total cost, and shipments are made over much greater distances. High-quality pumice is imported from foreign sources in crude form for processing domestically for abrasive purposes.

Greece and Italy have been important sources of imported pumice for many years. Unmanufactured pumice imports during 1963 valued at $15 per short ton or less, not including freight, were 6,345 tons from Italy valued at $54,000. Unmanufactured imports valued at more than $15 per ton were 1,230 tons valued at $30,000, all from Italy.

Wholly or partially manufactured pumice imports totaled 3,555 tons valued at $119,000. All of this was from Italy.

Imported abrasive-grade pumice is preferred by some users. Much of the low-cost imported pumice goes to the New England seaboard for use as a lightweight aggregate because the delivered cost is less than that for Western domestic pumice of similar quality.

The domestic duty for pumice per pound at the end of 1963 was: crude valued at $15 a short ton and under, 0.0425¢; crude valued over $15 a ton, 0.08¢; wholly or partly manufactured, 0.35¢.

STRATEGIC CONSIDERATIONS

The United States is considered to be self-sufficient in pumice supplies. During World War II no imports of Greek or Italian pumice were permitted, and although foreign pumice is claimed to be superior for some abrasive applications, there were no serious effects as a result of the embargo.

PRICES

There is a wide difference between the price of pumiceous materials suitable for abrasive purposes and that of those used for railroad ballast, road surfacing, and similar large-scale requirements. The price of domestically produced processed pumice in 1963, in ton lots, in bags, was $86 for fine and coarse ground, f.o.b. New York. During this period imported Italian, sundried, coarse and fine pumice, in bags, was $75 per short ton, f.o.b. New York.

TAXES

There are no special taxes imposed on the pumice industry. A 5-percent depletion allowance is permitted on domestic and foreign pumice operations.

TRANSPORTATION

Transportation cost is an important factor in the economics of the pumice industry. Abrasive grades can be shipped great distances to markets, even from foreign sources, but pumice of low-market value usually is limited to a few hundred miles by rail or truck. As ocean freight rates are less than land freight rates, oceanic shipments can be made over relatively longer distances.

RESEARCH

No comprehensive program of research on pumice has been announced. The relatively small income from most pumice operations makes it difficult to support a research program.

Publications outlining Government research in lightweight aggregates that involved pumice are shown in the references (*2*, *3*, *6*, *7*, *9*, *10*).

The Bureau of Reclamation and the U.S. Army Corps of Engineers conduct applied research on pozzolanic additives, including pumice, for cement.

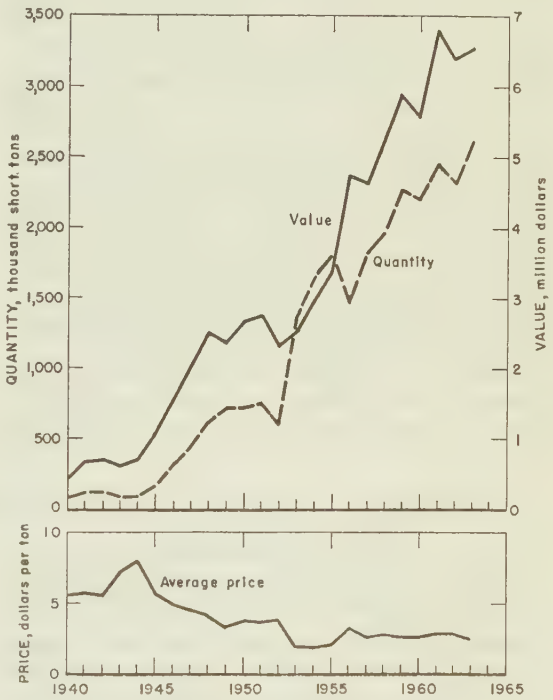

FIGURE 2.—Total Value, Quantity, and Average Price per Ton of Pumice.

OUTLOOK

Trends indicate that pumice production, during the 5-year period ending in 1969, may approach 16 million short tons compared with 12 million tons in the 1960–64 period.

With the rate of population growth increasing in the West and Southwest, local demand for pumice aggregate to be used in housing, roads, and industrial and commercial construction is expected to increase.

The results of studies made on the properties of lime-silica mixtures indicate a possible increase in use of pumice, pumicite, and volcanic

cinders as pozzolans in construction of dams and bridges.

The growth of manufacturing industries in the Western States may increase demand for the better grades of pumice used in scouring and rubbing blocks, as abrasives for glass and metal finishing, insecticide carriers, mechanics' soaps and paint fillers.

New deposits may be developed as demand increases, but exhaustion of present resources is not likely in the foreseeable future at present rate of consumption.

PROBLEMS

Specifications for pumice aggregates are not consistent but vary with different users; therefore, some producers or suppliers are required to stockpile excessive quantities of pumice materials to meet the various aggregate size requirements of consumers.

Production of uniform standardized pumiceous products is usually impractical because pumice from different deposits varies in physical characteristics. The lack of standardization in some areas tends to discourage the movement of pumice from one State to another, even though an interstate source may be within a more economical hauling range than the nearest intrastate source. Although some high-priced abrasive grades may be shipped long distances, the average value of most pumice is so low that high-shipping costs cannot be absorbed; thus the marketing area is restricted. Shipping distance for lower quality pumice used in road construction and as a lightweight aggregate is usually limited to only a few hundred miles and must compete with locally produced expanded clay, shale, or perlite, and slag or cinders.

Inasmuch as the product is sold at a low price, producers find it difficult to finance research that might increase usage or acceptability of the material. Technical information concerning mining, processing, and uses is limited or unavailable to some producers, and the growth of the industry is consequently limited.

Through research that has been done by some end-use industries, such as lime-silicate plants, additional problems have been noted:

(a) Some pumices have a flaky structure that makes them weaker and more absorptive than those having more normal vesicular form. This tends to promote higher shrinkage values and, in addition, the degree of fineness to which these pumices can be reduced for maximum strength and hydraulicity is limited.

(b) Absorption of moisture through hairline cracks between flakes and pores is a critical and undesirable characteristic, influencing changes during wetting and drying cycles. This excessive capacity for absorbing water possessed by pumice makes it difficult to use conventional concrete mix designs based on water-cement ratios.

(c) The small particle size and dusty nature of some pumices pose problems in the heat treatment process used to reduce or close pores and also presents a health hazard and a community nuisance problem.

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QUARTZ CRYSTAL

By Benjamin Petkof[1]

SINCE 1921 quartz crystal has been the preferred material for accurate frequency control in radio transmitters and many other electronic devices. These applications utilize the piezoelectric properties of quartz, by which a mechanical force produces an electrical charge and vice versa.

Thus, quartz crystal has become vital to civilian and military radio and communications activities. Its reliable frequency control and signal selection capability enable numerous radio transmitters to operate in narrow and crowded wavelength bands and multiple conversations to be carried on a single cable or carrier frequency.

Brazil is the only significant producer of optical and electronic quality natural quartz crystal. With technical and financial assistance from the United States during World War II, Brazil produced enough quartz crystal to meet U.S. requirements.

Since World War II the U.S. Army Signal Corps has sponsored and subsidized a comprehensive synthetic quartz crystal program in cooperation with industry and with private and government research organizations. Parallel studies of substitute materials have declined gradually in importance, and by 1958 the technical and commercial success of quartz crystal synthesis was assured.

The outlook is for expansion of industrial applications and a narrowing of the wide gap between peacetime and full mobilization requirements.

If manufactured electronic-grade quartz crystal replaces a substantial part of natural crystal for piezoelectric uses, complete self-sufficiency in all grades of clear quartz will require the establishment of domestic sources of suitable materials to replace Brazilian lasca, a byproduct of Brazilian electronic-grade quartz production now used in manufacturing fused quartz and as a nutrient for electronic-grade quartz synthesis.

BACKGROUND

The piezoelectric properties of quartz were discovered by Pierre and Jacques Curie in 1880–81. In 1917 Professor Langevin developed an ultrasonic submarine detection device for the French Navy, in which a generator of quartz crystal plates produced ultrasonic impulses. Although this submarine detector was not perfected until after World War I, this development stimulated interest in practical applications of ultrasonics and related phenomena.

In 1921 Professor Walter G. Cady of Wesleyan University, Middletown, Conn., discovered that quartz crystal could be used to control the frequency of radio oscillator circuits. A quartz plate of selected area and thickness serves as a piezoelectric resonator with a fixed mechanical vibration frequency that reacts electrically to control the frequency of the driving circuit (*2*, *9*).[2]

[1] Commodity specialist.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

PROCESSING INDUSTRY ORGANIZATION

Electronic-grade quartz crystals are consumed by producers of quartz plates and other forms for piezoelectric applications. At the peak of World War II demand, 113 quartz crystal processing plants were in operation. In 1963, 34 crystal cutters in 15 States reported consumption of 325,000 pounds of quartz crystals. Most cutters produced finished units, although some supplied blanks to other firms. A total of 13 million quartz piezoelectric units was made by 53 manufacturers.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

All crystalline materials lacking a center of symmetry are piezoelectric (*11*). Among such piezoelectric crystalline substances, quartz has

the highest known efficiency of transfer back and forth between strain and motion or from potential to kinetic energy.

Electronic-grade quartz crystal must be free from certain defects but not necessarily colorless. The smoky variety can be used for oscillators. If necessary to permit inspection, the color may be removed by heating to about 400° C, or windows may be trimmed in opposite sides of a surface-strained crystal to permit internal visual inspection.

The grading and classification of electronic- and optical-grade quartz crystal involve sorting according to size ranges, separation of faced and unfaced crystal, and estimation of the percentage of usable crystal by inspection and testing to detect and evaluate imperfections and flaws (*14*).

The defects in both electronic- and optical-grade quartz occur as optical twinning, cracks, inclusions, veils, bubbles, needles, ghosts or phantoms, and electrical twinning. An experienced inspector can detect optically all defects except electrical twinning when the crystals are properly illuminated in an oil bath having the same refractive index as quartz. Electrical twinning, however, can be inferred by surface irregularities in the crystals. Monochromatic polarized light is used to detect optical (crystallographic) twinning, and the other defects are detected with moderate arc-lamp illumination in the same oil bath. It is desirable to establish suitable facilities and acceptable inspection practices near the primary source of supply of raw quartz to reduce transportation on material that would be rejected by processors. Buyers of raw quartz for piezoelectric uses usually depend on visual- and oil-bath grading. Electrical twinning is normally detected in the early stages of manufacturing piezoelectric units by etching sawed surfaces with ammonium bifluoride or hydrofluoric acid.

National Stockpile Material Purchase Specification P–43 (September 12, 1951) provides 133 different categories for stockpiled crystals. Industry uses smaller crystals than are acceptable for the strategic stockpile. Most of the industrial consumption in 1963 was of crystals weighing less than 500 grams, and there was substantial consumption of quartz crystal weighing under 200 grams.

TECHNOLOGY

Geology

By far the greater part of the commercial deposits of electronic-grade quartz in the free world occurs in Brazil. The clear quartz crystals from which electronic-grade crystals are selected usually occur in vugs or pockets in deeply weathered quartz veins or in blanket deposits of milky quartz. The deposits are small and irregular and are distributed over a large area, principally in the States of Minas Gerais, Goiás, Bahía, and Pará. Very few single deposits produced more than 500 pounds of usable crystal per month during World War II. The ratio of eye-clear crystal to excavated material range from 1 : 1,000 to 1 : 100,000 (*10, 17*).

Present data indicate that the typical characteristics of the Brazilian deposits generally are applicable to quartz crystal deposits elsewhere.

Mining

Because of the irregular occurrence of quartz crystal deposits and the need to avoid damage to crystals by heavy blasting or rough handling, recovery has been restricted almost entirely to hand mining.

Marketing

Much of the quartz crystal in Brazil is bought by itinerant buyers who deal with individuals, small groups of primary producers, or local merchants. The itinerant buyers channel their purchases to exporters who use oil-bath grading to supplement visual observation. About 10 exporters handle most of the trade. Exporters who ship to the United States usually deal with an individual U.S. importing firm or have a U.S. affiliate or branch office.

Manufacturing of Quartz Crystal Units (*14*)

Before cutting, crystals are reexamined for optical and electrical twinning. Accepted crystals are oriented in a diamond saw frame, and oscillator wafers are cut along a predetermined crystallographic plane to a thickness slightly greater than the desired final thickness. Each wafer is inspected, defective areas are marked for removal, and the wafer is diced into blanks of the desired dimensions. The blanks then progress through a series of lapping stages until they reach the desired final thickness, and electrodes are attached. The finished plates are usually 0.25 to 0.75 inch in diameter and about 0.01 inch thick, and are mounted in suitable holders. The assembly is termed a quartz crystal unit and is ready for insertion in an electronic circuit.

USES

The major use of electronic-grade quartz crystal is for the production of crystal-controlled oscillator units to provide accurate

frequency control for radio transmitters, radio-frequency telephone circuits, and crystal-controlled chronograph and emission counters. Quartz crystal units also are used as wave filters in receiving circuits to exclude incoming signals of undesired frequencies. In other applications quartz and other piezoelectric materials are used electrostrictively as transducers to convert electrical forces into mechanical forces, as in loudspeakers and supersonic generators.

A small proportion of the reported imports of electronic-grade quartz crystal is used for prisms, wedges, lenses, and other optical purposes.

Lasca is used as the nutrient material for manufactured-quartz research and production. Selected quartzites, flints, and other highly siliceous materials are potentially suitable as nutrients for quartz crystal synthesis (*1*).

Plates of flawless natural quartz crystal are cut to predetermined axial orientations and used as seed plates to produce manufactured quartz.

Some quartz crystal is cut and polished for semiprecious gem stones. Clear stones, free from inclusions and flaws, are required for this purpose, but either type of twinning may be present.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

A small proportion of the reported imports of electronic-grade quartz crystal is classified as optical-grade quartz. Optical-grade quartz generally comprises the crystals of highest quality in the medium- to large-size groups. Electrical twinning is not harmful, but freedom from optical twinning, stains, inclusions, and other visual or crystallographic flaws is essential.

As of December 1958, fusing-grade quartz for the production of clear fused quartz (*6*, *21*) was obtained entirely by hand selection and hand trimming of rejects from the production of electronic-grade quartz crystal in Brazil. The material, known as lasca, must meet consumer specifications of size and visual appearance. The Lamp Division, General Electric Co., Nela Park, Cleveland, Ohio, in April 1957 supplied revised specifications covering two classes of crystals. In both classes crystals must be water white and have a median weight of 15 to 25 grams, with specific limits on the allowable percentage of larger and smaller sizes. Specifications for the two classes of crystals differ principally in the permissible content of visual defects.

ALTERNATE MATERIALS

In radio and television transmission, quartz is by far the best material for frequency-control oscillators. Synthetic ammonium dihydrogen phosphate has been used for, and is preferred in, sonar work; and synthetic ethylene diamine tartrate has been substituted successfully for quartz in telephone filters. However, the latter substitution is not completely satisfactory, and the trend toward the use of quartz in telephone filters has resumed. Other materials for specific applications are dipotassium tartrate, usable for oscillators and filters, and lithium sulfate monohydrate for ultrasonic applications.

In ultrasonic generators for industrial applications, quartz crystal does not hold the supremacy it enjoys in frequency-control devices (*11*). Ultrasonic sirens activated by compressed air are used widely in agglomerating and precipitating aerosols. Barium and other titanate ceramics are used in some applications, and ferromagnetic materials are used in others in place of quartz.

Small quantities of fused quartz have been used in Germany in place of optical-grade crystal in making optical prisms.

Tourmaline, nephelite, and various other minerals possess piezoelectric properties. None of suitable quality is commercially available, and none is as good as quartz for frequency control; however, some might be useful commercially if adequate supplies could be established.

MANUFACTURE OF QUARTZ CRYSTAL (*3–4, 7–9, 13, 15–16, 18–20*)

Quartz crystals are grown in autoclaves at pressures ranging from 1,500 to 20,000 pounds per square inch or more, and at temperatures of 250° to 450° C. Growth takes place on seed plates cut from natural or manufactured quartz in a predetermined crystallographic plane. The solution usually used is sodium carbonate. Brazilian lasca has been used as the nutrient in most of the experimental work and production in the United States. In England, however, some local quartzites and flints have been used successfully as nutrients (*1*). Quartz crystal containing defects is also usable.

In 1958 Sawyer Research Products, Inc., Eastlake, Ohio, began commercial production of manufactured quartz and in 1963 reported sales of 18,000 pounds to foreign and domestic users. Western Electric Co., North Andover, Mass., produces manufactured quartz for the Bell telephone systems.

It is estimated that 1 pound of manufactured quartz is equivalent to 3 to 4 pounds of natural

quartz of the qualities and sizes most commonly used by industry.

RESERVES

The quantity of quartz suitable for nutrient material for the production of manufactured quartz crystal is unlimited.

There are no domestic reserves of natural quartz crystal suitable for electronic use. Intensive field investigations during and after World War II revealed no deposits.

Brazil, the world's largest producer of quartz crystal, is thought to have large but undetermined reserves of natural quartz. The future development of these resources will be controlled by the country's internal political situation and world demand for high-quality electronic-grade crystal.

No other major world reserves are known. However, the U.S.S.R. and China are thought to have large reserves.

SOURCES OF STATISTICAL INFORMATION

The Bureau of Mines, through a canvass of importers and consumers of electronic-grade quartz crystal, obtains substantially complete data on the quantities of raw quartz consumed and the number of piezoelectric units produced. At intervals the Bureau obtains data from industry on the prices of quartz crystal and on progress in the output of synthetically produced quartz crystal.

The U.S. Department of Commerce compiles statistics on the quantity and declared value of imports of quartz crystal by country of origin, and on the declared value of exports and reexports of uncut and manufactured quartz crystal by country of destination. Lack of data on the quantity and quality of exports and reexports of uncut quartz crystal is the dominant factor in preventing reconciliation of consumption and imports for consumption.

PRODUCTION, CONSUMPTION, AND TRADE

As domestic production of electronic-grade quartz crystal is neglible, the United States is dependent on imports for its supply. The difference between imports and consumption represents rejections after reinspection, stockpiling, exports (unaccountable except for value), and small quantities used for optical and ornamental quartz (fig. 1).

The consumption of quartz crystal varies not only with the overall demand for quartz crystal piezoelectric units but also with the predominant types and sizes of units required and with industry practices regarding the use of large-

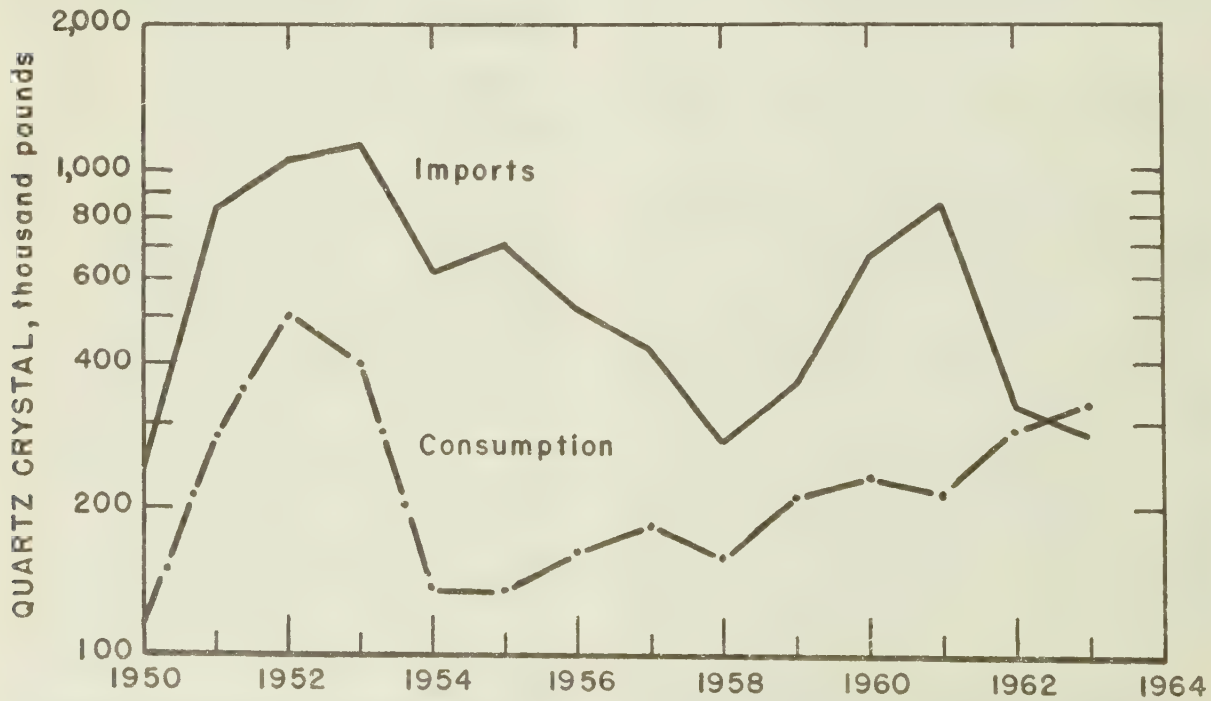

FIGURE 1.—U.S. Imports and Reported Consumption of Electronic- and Optical-Grade Quartz Crystal.

versus-small crystals. The number of piezoelectric units per pound of quartz, as reported by domestic consumers, fluctuated from 10.1 to 20.3 in 1942–50, from 11.7 to 33.6 in 1951–58, and from 28.6 to 43.4 in 1959–63.

Imports of electronic- and optical-grade quartz in 1963 totaled 282,176 pounds with a declared value of $446,719. About 99 percent of the imports of quartz crystal has come from Brazil. The remainder has come from the Malagasy Republic. Imports credited to France probably originated in the Malagasy Republic, and those credited to Japan originated principally in Brazil.

There is no tariff on imports of raw quartz crystal.

STRATEGIC CONSIDERATIONS

The U.S. quartz crystal fabricating industry has been completely dependent on foreign sources of raw quartz. The industry's dependence on imported material has decreased with the successful development of industrial methods for the manufacture of electronic-grade crystal. At the close of 1963 the total production capacity for manufactured quartz was estimated to be in excess of 70,000 pounds per year. This can be considered equivalent to about three times that quantity of natural quartz. Brazilian lasca has been used as nutrient material, but other varieties of quartz domestically available can be used.

The national stockpile of critical and strategic materials contains more than adequate stocks of natural quartz for use during any emergency. Inventories totaled 2,519 tons on June 30, 1964, of which 2,403 tons was in the national (strategic) stockpile, and 116 tons in the supplemental stockpile.

Brazilian production of natural quartz crystal is handicapped by remote sources, labor problems, and intricate political and commercial policies.

GOVERNMENT PROGRAMS

The Office of Minerals Exploration, U.S. Department of the Interior, will advance 50 percent of approved costs on exploration programs for electronic-grade quartz crystal.

PRICES

Electronic-grade quartz crystal is priced according to weight, percentage of usability, type and distribution of flaws, and whether faced or unfaced. From 1958 to the present, prices have shown only minor variation. However, price is subject to negotiation between the buyer and seller on the basis of quality. Table 1 provides current price information on the basis of weight classes.

TABLE 1.—*Price range per pound of electronic-grade quartz crystal by weight class*

Weight class (grams)	Price per pound	Weight class (grams)	Price per pound
100–200	$2.00–$3.50	501–700	$12.00–20.00
201–300	4.00–12.50	701–1,000	18.00–24.00
301–500	8.00–14.00	1,001–2,000	24.00–35.00

At present, manufactured quartz crystal is quoted at $27.50 per pound. Crystals can be grown to the buyers' size specifications.

TAXES

Producers are granted a depletion allowance of 23 percent on domestic production and 15 percent on foreign production.

RESEARCH

The U.S. Army Research and Development Laboratory, through contracts with industry, universities, and others, sponsored an extensive program to develop and evaluate manufactured quartz crystal from 1946 to 1964. The program reached its peak effort during 1954 and 1955. At present, effort is primarily concentrated on the further development of quartz crystal units using both natural and manufactured quartz. The Laboratory also evaluates prospector samples of domestic crystal.

During World War II the Bureau of Mines examined numerous quartz crystal deposits in the United States and published more than 70 reports covering field investigations on occurrences. Since World War II, Bureau activity on quartz crystal has been confined to the collection and dissemination of technical and statistical data.

OUTLOOK

The domestic quartz crystal fabricating industry has entered a period of transition from the complete use of natural quartz crystal to the partial use of manufactured quartz for the production of quartz elements. In 10 to 20 years manufactured quartz may completely displace natural quartz crystal as the fabricator's starting material. The development of faster growth rate, better quality, and higher *Q-factors* for manufactured quartz will tend to accelerate the transition.

Quartz crystal units will be produced in increasing numbers owing to the increasing requirements of the electronic and communications industries. The quantity of raw quartz consumed will remain stable or decrease because

of improved cutting techniques for both natural and manufactured quartz, and the continuing trend toward greater miniaturization of crystal units.

Natural quartz crystal imports should decline as manufactured quartz becomes more generally accepted by the industry. The lower price of natural quartz and its higher *Q-factor* will be offset by greater labor and cutting efficiency, higher cut-crystal yield, and future improvement of the *Q-factor* of manufactured materials.

Since 1958, the production and consumption of manufactured quartz has increased slowly. As industry obtains greater experience and know-how in utilizing this material, production and consumption will continue to increase although the rate of increase cannot be predicted. Plant production capacity will increase owing to new plant construction and the improvement of growth rate in existing plants. In several years, production capacity will reach about 100,000 pounds per year.

PROBLEMS

The unavailability of domestic sources of piezoelectric quartz has always been a primary problem. With increased use of manufactured quartz, this problem will become less important and may completely vanish.

Decreasing use of Brazilian quartz may cause decreases of the available supply of Brazilian lasca, which has been used as the feed material for the manufacture of cultured and fused quartz. Development of suitable domestic sources for these purposes will be necessary.

The continuing necessity for improving finished crystal units will require constant research. Changing operational specifications also will demand continual applied research in such areas as frequency variation with temperature, effect of small impurities in the crystal, radiation, and vibration effects.

The strategic stockpile contains an excess of about 4.4 million pounds of electronic-grade quartz. With improvements in the quality of manufactured quartz and the expansion of production capacity, revision of Government stockpile requirements for both quantity and quality will occur. Disposal of excess stockpile material at reasonable prices will be a major problem.

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RADIUM

By John G. Parker[1]

THE EXISTENCE of radium was first discovered by the Curies and G. Bémont. Several years later Mme. Curie isolated the first pure salt of radium and in 1910 she prepared the metal in cooperation with A. Debierne.

Pitchblende ore from Bohemia was the first source of radium, and Austria-Hungary was the main producer in the first decade of this century. From 1911 until the early 1920's, the United States was the major world producer of radium from Colorado Plateau carnotite deposits. U.S. production was curtailed by exploitation of high-grade pitchblende deposits in the former Belgian Congo. Belgium was the only primary radium producer until the 1930's when, through production from the Great Bear Lake pitchblende deposit in the Northwest Territories, Canada became a major supplier of radium. When Canadian production ceased about 10 years ago, Congolese pitchblende again became the principal source of radium. Although ore production was discontinued at the Shinkolobwe deposit in the Congo (Léopoldville) in 1960, radium-bearing slimes are still being processed in Belgium.

Radium has the distinctive property of emitting penetrating rays. It has been used by the medical profession in the treatment of cancer and by industry in radiography, in luminescent compounds, as a component of neutron sources for oil well logging, and in static elimination devices. In recent years competition from certain radioisotopes has increased greatly, but in some fields, especially in medical therapy, the long half life and radioactive spectrum of radium are its main advantages. However, radium has certain potential health hazards, and licensing of radium and inspection of facilities by various States are increasing.

BACKGROUND

Pierre Curie, Marie Curie, and G. Bémont discovered radium in 1898 while chemically treating pitchblende ore from the Joachimsthal silver mine in Bohemia, now the westernmost part of Czechoslovakia. In 1902 Mme. Curie isolated the first pure salt of radium—radium chloride—and in 1910 she and A. Debierne prepared the metal.

Joachimsthal was the main supplier during the early years of interest in radium. The ore was first processed for radium in France and shortly afterward in plants in Germany and in Austria. Because the Bohemian ores and plant were a monopoly of the Austro-Hungarian Government, the increasing interest in radium led to a worldwide search for other radium-bearing ores. Other foreign uranium mineral deposits from which radium was processed in this period are in Australia; Cornwall, England; the Malagasy Republic; Portugal; the U.S.S.R.; and the Republic of South Africa.

Although uranium minerals were discovered in Katanga in the former Belgian Congo in 1913, the first large production of radium-bearing ores outside Europe came from Colorado Plateau carnotite deposits in the United States, some of which had been mined years before. Beginning in 1911 Standard Chemical Co., Pittsburgh, Pa., exploited the U.S. ores, which were then shipped to France and to the Joachimsthal plant for treatment. By 1913 and 1914 several other companies had been formed and domestic processing plants had been started. To obtain supplies quickly for radium therapy, the Bureau of Mines entered into a cooperative agreement with the National Radium Institute in 1913 to study methods for producing and processing radioactive ores. By January 1917, shortly after the agreement expired, about 8,500 milligrams of radium had been extracted, processing costs had been greatly reduced, and methods for recovering by-product uranium and vanadium had been de-

[1] Commodity specialist.

veloped by Bureau technical personnel working at the plant erected by the Institute. The nearly 2,000 milligrams that had become the property of the Bureau of Mines was loaned to various medical and educational institutions until 1954, when most was transferred to the U.S. Atomic Energy Commission (AEC), Oak Ridge, Tenn.; the National Institutes of Health, Bethesda, Md.; and the National Bureau of Standards, Washington, D.C. A small quantity held in the Memorial Hospital, New York City, was recently transferred to the Public Health Service, U.S. Department of Health, Education, and Welfare, Washington, D.C.

The U.S. industry continued as the major supplier of radium until the early 1920's, at which time the rich Congolese uranium deposit at Shinkolobwe was exploited by Union Minière du Haut-Katanga. The refinery at Oolen, Belgium, which went into operation in 1922, produced radium so cheaply and abundantly that by 1925 all U.S. mining companies had ceased operations and Belgium was the only primary producer of radium.

Domestic radium refining has been sporadic, and production quantities have not been available since the early 1940's. Canadian Radium & Uranium Corp. operated a refinery at Mt. Kisco, N.Y., principally for secondary recovery, until about 1957.

With the discovery of pitchblende deposits at Great Bear Lake, Northwest Territories, in 1930 and the establishment of a refinery at Port Hope, Ontario, Canada became a major supplier of radium. A cartel agreement was soon reached between Belgian and Canadian producers to divide the world market on a 60–40 basis. The agreement was dissolved in 1941.

In 1939–40 Radium Chemical Co., Inc. of New York, the sales representative of Union Minière, imported enough pitchblende ore from Belgium to supply U.S. and Canadian refineries with raw material for 100 grams of radium, believed to be enough for the wartime emergency. Early atomic research by the Manhattan Project during World War II depended partly on this supply of 1,200 tons of stockpiled pitchblende ore. In addition, other Congolese ores were shipped directly from Africa to North America by fast freighters for refining, primarily for their uranium content. The war years were the last for the Canadian producer, Eldorado Mining & Refining, Ltd. which sold all stocks of refined radium to Atomic Energy of Canada, Ltd. in 1955. Since then, most primary radium has been derived from Congolese pitchblende ores processed at the Oolen, Belgium, refinery.

GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

The principal domestic suppliers of radium and its compounds are the Canadian Radium & Uranium Division, Canrad Precision Industries, Inc., New York, N.Y.; Radium Chemical Co., Inc., New York, N.Y., the U.S. outlet for radium recovered and refined by the Belgian firm Union Minière du Haut-Katanga; United States Radium Corp., Morristown, N.J.; and A. Bruce Edwards, Bala-Cynwyd, Pa., sales representative for Atomic Energy of Canada, Ltd., Ottawa, Ontario, Canada.

Stocks of Congolese pitchblende concentrates and radium-bearing slimes produced prior to April 1960 by Union Minière are processed by Société Générale Métallurgiques de Hoboken at its refinery in Oolen, Belgium.

DEFINITION OF TERMS (*11*) [2]

The importance of radium and similar elements is due to their emission of rays or radiations. Radium and its related elements are unstable, implying that the nucleus of the element is capable of changing by emitting one or more of its particles or rays. The particles or rays emitted by unstable nuclei are called nuclear radiation, and atoms that give off such radiations are called radioactive.

Radiation intimately related to radium are alpha particles, beta particles, and gamma rays.

An *alpha particle* is identical with a helium nucleus. Although these particles are so small that 1×10^{20} of them are about as large as the head of a pin, they are the largest electrically charged particles known. They constitute the emission of major importance in radium but have little penetrating power; a few inches of air or a sheet of paper will stop them.

Beta particles, about 1/7200 as large as alpha particles, are identical with electrically negative electrons which can travel several yards through air and penetrate as much as one-third inch of body tissue.

Gamma rays are not particulate in nature but are electromagnetic radiations of high energy originating in atomic nuclei. They are physically the same as high-energy X-rays, can travel hundreds of feet through air, and are capable of penetrating many inches of almost any type of solid material. Radium emits small quantities of gamma rays, mostly from the beta-gamma decay of daughter elements radium B (lead 214) and radium C (bismuth 214).

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

Neutrons are particles about one-fourth the size of alpha particles. Because they have no electrical charge, they can travel many feet through solid matter and hundreds of feet through air.

Radioactive transformations of unstable elements, resulting in their breakdown into new elements possessing different chemical properties, are caused primarily by the emission of alpha and beta particles. Such newly formed atoms are called decay products or daughter elements. In the three natural radioactive disintegration series they are unstable, forming other daughter elements, the end product being a stable isotope of lead. With radium 226 (atomic weight 226.0), the most common form of the element, the first decay product is radon (atomic weight 222). Radon is transformed into radium A (atomic weight 218) which decays to radium B (atomic weight 214) and so on until stable radium G, corresponding to lead 206 (atomic weight 206), is reached.

The *half life* of any particular radioisotope is the time required for the radioactivity of a given quantity of the isotope to decrease (or decay) to half of its original value. Radium 226, the most abundant isotope of the element, has a half life of over 1,600 years. Its very small annual decay or loss of about 0.04 percent is of great consequence in considering the usefulness of radium 226 in medical therapy.

A *curie*, named in honor of the Curies, is defined as the quantity of any radioactive species in which 3.7×10^{10} nuclear disintegrations occur per second. It is also defined as the activity associated with 1 gram of radium.

The name *curietherapy* has been applied to the use of radium for therapeutic purposes by the medical profession; the prefix *tele-* is added to indicate radium therapy from an exterior source not in physical contact with body tissues. Curietherapeutic dosage is expressed as the quantity of radiation received by the tissues. The *exposure dose*, expressed in roentgens, is a measure of the total ionization that the quantity of radiation could produce in air. This differs from the *absorbed dose*, usually expressed as rads, which represents the energy absorbed from the radiation per gram of specified body tissue.

Maximum permissible dose may be defined as the limit of radiation exposure below which no noticeable harm is expected for a person receiving it regularly over a lifetime (*1*).

Radium preparations, after measurement at an official institute possessing a primary or secondary standard, are sold on the basis of the quantity of the element present.

Two primary standards for determining radium content have been established. The first official International Standard was prepared by Mme. Curie in 1912 for deposit at the International Bureau of Weights and Measures at Sevres, France, and contains 21.99 mg of pure anhydrous radium chloride. The second International Standard was prepared in Austria and serves as a Reserve International Standard; it contains 31.17 mg of pure anhydrous radium chloride. Secondary standards, calibrated with the International Standard at Sevres, are employed in routine measurements. The National Bureau of Standards, Washington, D.C., has a secondary standard (*10*).

TECHNOLOGY

The extraction of radium from uranium ores has presented unusual problems because of the extremely small proportion of radium present. Bureau of Mines researchers often had to treat 200 tons of ore to obtain 1 gram of radium, a yield of 1 part in 180 million (*2–3*, *9*).

In recent years, the Congo (Léopoldville) has been the source of most primary radium. The direct acid leaching method used in opening Congolese pitchblende ore and subsequent processing of the enriched slimes at Oolen, Belgium, may be considered the most important industrial technique. Other pitchblende digestion processes consisted of the original Curie sodium sulfate fusion technique used on the Joachimsthal (Czech) ores, the modified Curie process of initially roasting the ore with sodium carbonate and nitrate, leaching Cornish (English) ores with hydrochloric acid, and oxidizing and chloridizing the more complex Eldorado (Canadian) ores by roasting followed by sulfuric acid leaching.

A different method used for the digestion of carnotite ore involved heating pulverized mineral with 80 percent sulfuric acid, then filtering through glass wool and allowing to cool. The result was the deposition of barium, previously added as a carrier for radium, and radium sulfates (*5*). In all cases, a residue of barium-lead-radium sulfate remains after the uranium is removed. This residue, called "white cake," often contains a significant quantity of silica and usually is subjected to sodium chloride leach for 3 to 4 hours to remove the bulk of the lead. The rest of the lead sulfate, silica, and mixed barium-radium sulfate in the residue is carbonated with soda ash (Na_2CO_3), which is subsequently washed free. The resulting carbonate cake is dissolved in hydrochloric acid, and the washed chloride filtrate, treated with excess sulfuric acid, forms a sulfate cake which is washed free of acid. Another carbonating step ensues and, with subsequent removal of the carbonate ion by washing, a reaction of the car-

780–887 O—65——48

bonate with hydrobromic acid provides a filtrate of barium-radium bromide and lead bromide. The last technique of fractional crystallization takes advantage of the relative enrichment of radium to that of barium in the crystal phase and, with many successive fractional crystallizations, more than 90-percent-pure radium bromide crystals may be produced (*6*). Ion exchange and solvent extraction with chelating agents have been used to separate radium from barium. Ion-exchange methods using synthetic organic resins reportedly afford complete separation of these elements. The resin is degraded by intense radiation from larger quantities of radium, with resulting formation of insoluble radium compounds in the ion-exchange column (*4*). Radium metal may be produced by electrolysis of the bromide in an aqueous solution, using a mercury cathode (*5*), and from a radium chloride solution using a mercury cathode and a platinum-iridium anode. A residue of pure radium metal is then obtained from the amalgam by thermal decomposition in a hydrogen atmosphere (*4*).

Secondary radium has been reclaimed domestically from old capsules and other applicators.

USES

The most important application for radium has been in medicine, particularly in cancer treatment. Radium as a salt sealed in tubes and needles is used directly in curietherapy and has been used in radium bombs in telecurietherapy. Radon, a daughter element of radium with a short half life, is compressed in small capsules, usually gold seeds, and is used principally for implants in tissue (*6*).

During World War II several hundred grams of radium were reportedly used in luminescent compounds. Mixed in small quantities with compounds such as zinc sulfide, radium is the activating component in self-luminous paint for dials of watches and instruments and for signs (*8*). Radium, usually in the form of the insoluble sulfate in gastight metal containers, is used in industrial radiography, particularly in nondestructive inspection of metal castings. Because of the high specific ionizing power of its alpha particle emission, radium has been used in devices to dissipate hazardous static electricity. The alpha particles are responsible also for the alpha-neutron reaction in beryllium compounds used as moderately intense neutron sources in oil well logging and as initiators of nuclear reactions in atomic reactors. Advantages of radium over most of its alternate materials are its long half life and stability in a fission process.

COPRODUCTS AND RELATIONSHIP TO OTHER COMMODITIES

Although radium is always associated with uranium, only a few uranium-bearing mineral deposits were sufficiently enriched to permit mining solely for radium. Pitchblende, a variety of the uranium oxide, uraninite, and canotite, a hydrated potassium-uranium vanadate of secondary origin, have been the major ore minerals of radium.

The more important decay products of radium are radium emanation (radon, a heavy inert gas), radium A, radium B, and radium C, with respective half life values of 3.825 days, 3.05 minutes, 26.8 minutes, and 19.7 minutes. These daughter products are useful in curietherapy but are of concern as health hazards. Other decay products are radium C′, radium C″, radium D, radium E, radium E″, radium F, and radium G, which is the stable end product chemically identical with lead (atomic weight 206).

Radioactive substances used in radium therapy include principally radon and radium sulfate, rarely radium bromide and chloride.

ALTERNATE MATERIALS

Many radioisotopes have been produced and marketed by AEC and have become available from private concerns. They are largely decay products, obtained from nuclear reactors, which are processed relatively cheaply and can be substituted for radium in a number of applications because of their similar radiation spectra. In the United States approximately 100 radioisotopes are now available from the AEC, compared with 4 in 1946, and about 30 can be purchased at reasonable terms from private firms. In the spring of 1964, cobalt 60 was being produced by at least eight of these companies.

Although only a relatively few of these isotopes can be used instead of radium, one of the most important—cobalt 60—has a large usage in industrial radiography and is being used increasingly in medical therapy. It has considerable usage in teletherapy, a field in which X-ray equipment is also of great value. Although radium formerly was dominant in medical therapy, tubes and needles of gold 198, cobalt 60, and cesium 137 are now being used as interstitial implants and intracavitary appliances. Many physicians and other medical personnel still prefer radium in sealed sources because of its long half life and because they are more familiar with its dosimetry and treatment techniques. In alpha sources and foils ameri-

cium 241 has a fairly long half life and is less subject to leakage than is radium 226. In addition to cobalt 60, high-voltage X-ray machines and such radioisotopes as cesium 137, iridium 192, and thulium 170 are used in industrial radiography. Luminescent compounds activated with beta emitters, hydrogen 3 (tritium) and krypton 85, reportedly reduce health hazards and deterioration and afford a constant-level, longer lived light output. Static elimination devices now usually contain americium, polonium, or krypton 85.

In neutron sources, mixtures of americium 241, polonium, plutonium, actinium 227, lead 210, antimony 124, or thorium 228 with beryllium metal can be used instead of beryllium-radium mixtures.

TABLE 1.—*U.S. imports for consumption of radium salts, radioactive substitutes, and useful radioactive substances*

Year	Radium salts [1]		Radioactive substitutes,[2] value (thousands)	Useful radioactive substances,[3] value (thousands)
	Milligrams	Value (thousands)		
1954–58 (average)	56,254	$813	[4] $521	
1959	32,967	518	1,145	
1960	23,333	364	1,394	
1961	12,947	185	1,509	
1962	46,962	700	1,732	
1963:				
January–August	44,660	304	1,081	
September–December				$426

[1] Data no longer separately classified beginning Sept. 1, 1963, included with useful radioactive substances.
[2] Includes artificial radioactive isotopes that are not substitutes for radium.
[3] Due to changes in classification by the Bureau of the Census, Sept. 1, 1963, these include elements, isotopes, and compounds, except natural metallic thorium and uranium and their compounds.
[4] Due to changes in tabulating procedures by the Bureau of the Census, data known not to be comparable with other years.

SOURCE: Bureau of the Census, U.S. Department of Commerce.

RESERVES

Although radium was extracted formerly as a primary product from high-grade Colorado Plateau carnotite ores, in a sense there are currently no domestic mineral reserves of radium. Cessation of domestic production, brought about largely by competition from richer foreign sources, placed all domestic radium ores below the economic and technologic margin. The geochemical abundance of radium in rocks is seldom greater than 1 part per trillion (1×10^{-6} grams per ton), but the greatest enrichment is in granitic rocks. The commercial occurrences are in uranium ore deposits in which radium occurs with uranium in a ratio of 1 to approximately 3 million. Congolese ores from the rich Shinkolobwe pitchblende deposit are the source of most of the radium processed in recent years, but quantitative figures are lacking (*7*).

SOURCES OF STATISTICAL INFORMATION

Statistical information is obtained from the four companies or agents dealing in or producing radium and radium-bearing devices, from the weekly publication "Steel," from the Bureau of the Census, U.S. Department of Commerce, and from the annual reports of the Union Minière du Haut-Katanga.

PRODUCTION, CONSUMPTION, AND TRADE

No domestic production has been reported for a number of years, and over 75 percent of the radium salts imported in the last 10 years has been recovered from Congolese uranium ores at the Belgian radium refinery at Oolen.

The total production of radium is probably less than that of any other naturally occurring element. Since the first separation by the Curies in 1898 the annual world production of radium has fluctuated widely. Data for years of higher production during World War II are not available because of security reasons or because of company confidential figures. The U.S. domestic industry was at its peak in 1921 when radium salts were produced by five companies. Within 2 years, under the impact of Congolese radium, only United States Radium Corp. was isolating radium and by 1925 even this company had ceased production. Total production of radium in Colorado has been valued at $20 million. In 1964 it was estimated that the total world radium stock was about 3,000 grams, about 500 grams of which is in the United States.

From 1954 to 1963, about 65 percent by weight and 48 percent by value of U.S. exports of radium metal and alloys were shipped to Canada. Significant quantities were sent to Brazil, Libya, Switzerland, and Norway; lesser quantities were shipped to Venezuela, Italy, France, Belgium, the Netherlands, West Germany, Surinam, and Argentina. Canada has been the only consistent consignee of radium metal and alloys, averaging $16.58 per milligram which is about $6 less than the 10-year average for all these exports. Other high prices for material shipped to countries such as Italy and the Netherlands are due probably to the costs of new radium and new or expensive encapsulation.

Imports of radium salts during the period were received mostly from Belgium, with Canada supplying most of the remainder. The United Kingdom, the Netherlands, and Colom-

bia were the only other countries shipping any significant quantities. Low unit prices for some imports usually reflect reprocessing costs for old radium.

No rates of duty apply to imports of radium and radium salts or to the new inclusive tariff classification listed under item 494.5000 of the 1963 tariff schedule. Under the new tariff classification, however, it is impossible to differentiate radium from radioactive isotopes.

STRATEGIC CONSIDERATIONS

Demand for radium, considerably lessened by the impact of radioactive isotope substitutes, could be met from byproduct radium extracted from uranium-mill wastes or by recovery of secondary radium. Strategic and defense needs for luminescent materials are being satisfied increasingly by less hazardous luminescent materials activated with radioisotopes and by devices recently developed for seeing at night.

GOVERNMENT PROGRAMS

Radium has had increasingly strong competition in recent years from the radioisotopes which have become increasingly available under the production and distribution program conducted by AEC. A depletion allowance of 15 percent is still available on gross incomes from mining both domestic and foreign radium-bearing minerals.

PRICES

Radium is still the highest priced of all metal commodities. Although the quoted price in "Steel" and in E&MJ Metal & Mineral Markets has remained stationary for about 10 years, recently gram quantities of old or used radium have been sold for as little as $2 per milligram, equivalent to $1 million per pound. This is in strong contrast to the quoted market price of $16 to $21.50 per milligram of the metal in purified salts, dependent upon quantity. It is even further from the price of $120 per milligram for the first commercial radium and the peak price of $180 per milligram in effect just prior to World War I. For 10 years starting with 1953, the Bureau of the Census data indicate that the average of declared prices for radium-salt imports remained somewhat below the lowest quoted price but, in 1963, the average of declared prices dropped to less than half of those quoted, largely owing to the influx of low-priced imports from Canada and the United Kingdom. These anomalous prices do not pertain to primary uranium, and probably are reprocessing charges for secondary radium or reencapsulating of radium from old sources.

RESEARCH

Recently radium investigations have centered mostly on ascertaining health hazards and genetic results associated with the use of radium, improving methods for determining radium in various materials and in different environments, devising separatory techniques for the element, evaluating its therapeutic effects, devising better applicators, providing satisfactory storage facilities, and promoting better handling procedures. As shown in "Nuclear Science Abstracts," research is being conducted in the United States and in numerous European countries by national, State, and private laboratories, by cancer research institutes and hospitals, by universities, and by units working under various Government atomic energy commissions and authorities.

OUTLOOK

Primary radium, obtained mostly from Belgian and to a lesser extent from domestic company stocks, as well as some reclaimed radium, is adequate to meet anticipated requirements. A number of States which have recently assumed control of regulatory authority in the field of radiation hazards, a function formerly administered exclusively by AEC, make no discrimination in licensing between radium and radioisotopes. This has the effect of removing radium from its preferred status of ready availability, thereby encouraging more interest in and increased use of radioisotopes for former radium applications.

Radium will continue to be preferred in certain applications, principally in medical therapeutic uses in which its long half life allows storage for years with little change in radiation characteristics.

Conversely, certain health hazards connected with the use of radium may differ in comparison with those of radioisotopes.

PROBLEMS

Competition with increasingly abundant radioisotopes having distinctive radiation properties and available at lower prices is reducing the demand for radium.

Telecurietherapy, industrial radiography, and luminous compounds are requiring increasingly larger quantities of radioisotopes.

In common with other waste products from uranium processing plants, radium has caused water pollution. Other health hazards have been caused by improper handling and storage of the small containers of radium salts used in medical therapy and radiography. Also, workers preparing luminous compounds containing radium salts sometimes are subject to ingestion or inhalation of particles or radon in quantities greater than the maximum permissible concentration. A number of States still do not exercise a strict control over the use of radium.

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RARE-EARTH ELEMENTS

By John G. Parker [1]

IN THIS chapter, the rare-earth metal group is considered to include the series of 15 chemically similar elements with atomic numbers 57, lanthanum, through 71, lutetium.

The term rare earths was applied to the oxides of the elements because of their apparent scarcity and their resemblance to the alkaline-earth oxides. Some scientists prefer the terms lanthanides or lanthanons. Industry, however, through long usage, favors the term "rare earths," often including the elements yttrium and sometimes scandium.

Monazite and bastnaesite are the principal commercial rare-earth ore minerals. Euxenite, mined in the 1950's for its columbium, tantalum, and uranium, yielded rare-earth byproducts enriched in elements of the heavy rare-earth subgroup. Apparent domestic production of concentrates in 1963 was nearly 2,350 tons of contained rare-earth oxides. Most of this was derived from imported and domestic monazite processed for its rare-earth element and thorium content. The remainder has been processed from bastnaesite shipped increasingly in recent years from the world's largest known rare-earth mineral deposit in California.

Rare-earth mineral concentrates usually are processed first to rare-earth sodium sulfate by digesting with sulfuric acid. This double salt is converted to other salts such as the chlorides, oxides, fluorides, nitrates, and carbonates. Alternatively the caustic soda method initially produces rare-earth and thorium hydroxides and byproduct trisodium phosphate. The crude salts produced from either method are used directly or may be converted into higher purity compounds. Rare-earth chloride can be electrolyzed into misch metal. Part of the crude production is separated into cerium, lanthanum, or didymium portions before further processing into metals or salts. A solid-state process has been developed to convert bastnaesite to an oxide polishing compound by roasting. Ion-exchange and solvent-extraction techniques are employed in separating the rare-earth elements and are greatly superior to older fractional-crystallization methods in most instances. In the form of metal or alloy, such as misch metal, cerium metal, and ferrocerium, rare-earth elements are used mostly in lighter flints or sparking metal; as deoxidizers, scavengers, and grain refiners in steel and other ferrous alloys; as nodularizers in certain types of cast iron; and as promoters of high strength and creep resistance at elevated temperatures in aluminum and magnesium alloys.

Rare-earth compounds find wide use as superior glass polishing powders and as glass colorants and decolorizers. The oxides and fluorides are used in the cores of arc-light carbons in searchlights and for high light intensity with good color balance in motion pictures. Newer or potential applications are as preventers of deterioration caused by ultra-violet light in some foods in glass containers and as photochromic materials in variable-transmission glass windows, as invaluable components in phosphors used in color television tubes, as activating dopants in materials used for laser research, and as control rod materials in nuclear reactors.

The outlook for the industry is for steady growth, especially for production of materials used by the glass and metals industry and of high-purity compounds and metals for newer or potential uses. Any of several recent discoveries concerning light absorption and fluorescence phenomena could bring about a rapid increase in consumption of certain rare-earth compounds. Partly affecting these potential uses is the availability of heavy subgroup elements from less common ores, such as euxenite and xenotime, and as byproducts from other mining ventures.

The principal problems of the industry are created by oversupply of certain byproduct rare-earth elements which necessitates intensi-

[1] Commodity specialist.

fied utilization and market research. On the other hand, determination of unusual properties of very high purity rare-earth metals and compounds and better knowledge of new sources, extraction, separation, and metal reduction procedures are necessary for a broader base upon which to establish the foundation of newer portions of the rare-earth industry. Many research institutions, much of the industry, and a number of Federal agencies including the Bureau of Mines are conducting research on rare-earth metals and compounds.

BACKGROUND

The first recorded domestic shipment of monazite was in 1887 from Burke County, N.C. Production reached a peak of 787 tons in 1895 and averaged 300 short tons per year through 1910. German firms dominated the production of thorium nitrate from monazite mined in Brazil and in India. Mine production started in Brazil in 1895 and in India in 1911. Because the average thorium oxide content of monazite from the Carolinas was only 3.5 to 4 percent while that from Brazil and India averaged 6 and 8 percent, respectively, domestic producers found it difficult to compete. Consequently, German manufacturers soon built up an almost complete monopoly of the thorium nitrate industry. As a result, the total domestic output of monazite from 1911 through 1947 was only about 50 tons. Larger quantities of monazite were produced from 1948 through 1963. In 1949, bastnaesite, a mineralogical curiosity until that time, was discovered in large quantities in the Mountain Pass, Calif., district in carbonate rocks cutting a metamorphic complex. Production at and shipments of rare-earth mineral concentrates from the site have increased in recent years.

The domestic industry has grown from a few small, closely held companies that started using thorium nitrate in the manufacture of incandescent gas mantles around 1900. At first, most of the thorium nitrate was imported from Germany, but World War I forced the companies to process monazite from Brazil and India. Initially, the rare-earth metals produced as byproducts from the monazite were of little value, but uses for them were found. As electric lights replaced gas mantles, monazite was then processed for over a score of years mainly for its rare-earth content. After World War II, the situation was reversed, and monazite was again produced largely for thorium. Moreover, the rapid advances in science and technology after World War II indicated that the rare-earth metals had important industrial uses, and the discovery of large deposits made the term "rare" a misnomer. The result was that in the early 1950's interest in the rare-earth metals was stimulated, and the industry expanded. Early enthusiasm proved unwarranted, but through corporate consolidations a stable industry was developed to undertake solution of the many problems confronting development of rare-earth resources.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Since 1955 rare-earth minerals have been mined sporadically in at least eight States. Bastnaesite concentrate has been produced since 1952 by Molybdenum Corp. of America at its mine and beneficiation plant at Mountain Pass, San Bernardino County, Calif. In 1956, bastnaesite was shipped from a mine in Lincoln County, N. Mex., operated by New Mexico Copper Corp. Monazite dredging operations in the middle 1950's in Valley County, Idaho, by Baumhoff-Marshall, Inc., and Idaho-Canadian Dredging Co. were extended into 1959 by Baumhoff-Marshall and later by J. R. Simplot Co. Through 1959 Porter Bros. Corp. dredged euxenite in Valley County, Idaho, principally for its columbium-tantalum and uranium content with byproduct recovery of rare-earth elements of the heavy subgroup. The only current production of monazite is from dredging in Duval County, Fla., where Titanium Alloy Manufacturing Division of National Lead Co. recovers it as a byproduct of ilmenite and rutile.

The principal chemical processors of concentrates and producers of rare-earth compounds, including sulfates, oxides, chlorides, fluorides, nitrates, and other salts of mixed and individual rare-earth elements, are as follows: Rare Earth Division, American Potash & Chemical Corp., West Chicago, Ill.; Davison Chemical Division, W. R. Grace & Co., Pompton Plains, N.J.; Lunex Co., Pleasant Valley, Iowa; Michigan Chemical Corp., St. Louis, Mich.; Molybdenum Corp. of America, York, Pa.; Research Chemicals Division, Nuclear Corp. of America, Phoenix, Ariz.; and Vitro Chemical Co., Chattanooga, Tenn.

Metals and alloys such as misch metal are produced from individual or mixed rare-earth chlorides or fluorides purchased from the chemical processors. Some of the latter, including American Potash & Chemical Corp. and Michigan

Chemical Corp., also produce high-purity metals. Research Chemicals Division and Lunex Co. are principally refiners and producers of high-purity compounds and metals. The principal producers of misch metal and ferrocerium (lighter flints) are Ronson Metals Corp., Newark, N.J. and American Metallurgical Products Co., Inc., New Castle, Pa. Vanadium Corp. of America, Union Carbide Corp., and Vitro Chemical Co. manufacture rare-earth-bearing silicon alloys.

In Brazil, rare-earth chlorides and other mixed rare-earth compounds are processed principally by Orquima Industrias Quimicas Reunidas, S.A., from monazite sands extracted from beach sand deposits in the States of Bahia, Rio de Janeiro, and Espirito Santo. Monazite is extracted from black sands in the States of Kerala and Madras in the southwestern part of India and processed at a plant in Alwaye operated by Indian Rare Earths Ltd., Bombay, for the Indian and Kerala Governments. Europe and Japan are the chief markets for most of the rare-earth materials produced by the Indian and Brazilian processors. A large vein monazite deposit at Van Rhynsdorp, Republic of South Africa, has provided large tonnages to the United States until recently. After having been closed since March 1959, it reopened again early in 1962 and supplied a large quantity of monazite to an American processor, again closing down in the middle of 1963. Monazite has been recovered increasingly, since the first production in 1948, from Australian beach sands which apparently will become one of the major sources now that the South African production has ceased. The Malagasy Republic, also one of the larger suppliers of monazite concentrate, has a large concentration plant operated by the French Atomic Energy Commission and Pechiney at Antete which has been increasing production in recent years. Byproduct production of monazite from alluvial tin mining takes place in Indonesia and Malaysia. Other less important monazite sand deposits have been worked in Ceylon, Korea, Nigeria, and Egypt.

Foreign companies which process rare-earth mineral concentrates and produce compounds include—Treibacher Chemische Werke A.G., Treibach, Austria; Orquima Industrias Quimicas Reunidas, S.A., Sao Paulo, Brazil; Johnson Matthey & Co., Ltd. and Thorium Ltd., London, England; Typpi Oy, Oulu, Finland; Société Pechiney-St. Gobain, Paris, France; Th. Goldschmidt A.G., Essen, West Germany; Indian Rare Earths, Ltd., Alwaye, India; and Santoku Metal Industry Co., Kobe, Japan. The Finnish company has a unique plant that was established in 1963 to extract the rare-earth elements contained in apatite.

Misch metal and other rare-earth metals and alloys are produced by the following foreign firms: Treibacher Chemische Werke A.G.; British Flint & Cerium Manufacturing, Ltd., Kent, England; Société Pechiney-St. Gobain and Société Kuhlman, Paris, and Société d'Electrochimie du Centre, Dijon, France; Th. Goldschmidt A.G., Essen, and Prometheus Metallwerke, Kempten, West Germany; and Santoku Metal Industry Co., Kobe, and Ogino Chemical Institute, Hyogo, Japan.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Webster's New Collegiate Dictionary (1960) defines "*rare earth*" as "any of a series of very similar oxides of the rare-earth elements," and "rare-earth element or metal" as "any of a group of very similar elements of successive atomic numbers, beginning with cerium 58 (sometimes with lanthanum 57) and extending through lutecium [sic] 71." In this chapter and in most commercial and scientific usage the rare-earth metals are taken to be the 15-element group from atomic number 57 through 71. In commercial usage the group is frequently expanded to include yttrium, atomic number 39, and occasionally to include scandium, atomic number 21. The rare-earth group also is referred to scientifically as the *lanthanides*; or, less commonly, as the *lanthanons*, terms proposed by the chemists V. M. Goldschmidt and J. K. Marsh. The scientific grouping of rare-earth elements is based on a characteristic known as the *lanthanide contraction*. As a result of the lanthanide contraction changes in the atomic structure as the atomic number increases do not strongly affect the valence force between atoms. This accounts for the striking similarity in chemical behavior of the elements within the group. Scientists use the term *actinide rare earths* for the group of 15 elements from atomic number 89 through 103 in the periodic table. These are chemically similar radioactive elements and comprise a distinct group unrelated to the rare-earth elements.

The rare-earth metal group name was assigned when the elements were considered to be scarce and because of the earthy appearance of their oxides. It is now realized that these elements as a whole are actually more abundant than many better known and commonly available elements.

Writings on the rare-earth elements and compounds are confused by frequent use of the term "rare earth," without a hyphen, to mean different things. (*3, 9, 19*).[2] As a noun the term is

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

used to mean both an element and the oxide of an element. As an adjective, the term frequently is used without the proper accompanying noun, sometimes confronting the reader with an ambiguous expression. For specificity of language the present discussion follows Webster in using the hyphenated adjective form, such as, *rare-earth elements*, *rare-earth minerals*, *rare-earth metals*, or the redundant *rare-earth oxides*. Sometimes when referring to the individual oxides the suffix *-a* may be used to replace *-um*, for example in *ceria*, *gadolinia*, and *samaria*.

Sufficient differences have been found to permit classifying the rare-earth elements into subgroups, based on their chemical behavior. Current practice is to break the 15 successive elements plus yttrium into a *light* and *heavy subgroup*. The light subgroup incorporates the elements from lanthanum through europium and the heavy subgroup, from gadolinium through lutetium plus yttrium (*22*). They are also called the *cerium* and *yttrium* subgroups after the most abundant elements which they contain. Some researchers have used a tripartite division into a *cerium subgroup* of elements with atomic numbers 57 through 62; a *terbium subgroup*, numbers 63 through 66; and an *yttrium subgroup*, with yttrium and elements with numbers 67 through 71 (*15*). Some properties of the rare-earth elements are shown in table 1.

TABLE 1.—*Selected properties of the rare-earth metals*

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Atomic number [1]	57	58	59	60	62	63	64	65	66	67	68	69	70	71
Atomic weight	138.92	140.13	140.92	144.27	150.35	152.0	157.26	158.93	162.51	164.94	167.27	168.94	173.04	174.99
Estimated abundance [2] ppm	5–18	20–46	3.5–5.5	12–24	4.5–7	0.14–1.1	4.5–6.4	0.7–1	4.5–7.5	0.7–1.2	2.5–6.5	0.2–1	2.7–8	0.8–1.7
Crystal structure (at room temperature) [2 3]	Hex	Fcc	Hex	Hex	Rhomb	Bcc	Hcp	Hcp	Hcp	Hcp	Hcp	Hcp	Fcc	Hcp
Density (at room temperature) [2] g/cm³	6.174	6.771	6.782	7.004	7.536	5.259	7.895	8.272	8.536	8.803	9.051	9.332	6.977	9.842
Hardness (Rockwell) [4]	55	3	38	50	63	26	67	62	57	57	63	69	−4	86
Melting point [2] °C	920	794	935	1,024	1,072	826	1,312	1,356	1,407	1,461	1,497	1,545	824	1,652
Boiling point [4] °C	3,470	3,470	3,017	3,210	1,670	1,430	2,800	2,480	2,330	2,490	2,420	1,720	1,320	3,000
Mean metallic radius Å	1.877	1.825	1.828	1.821	1.802	2.042	1.802	1.782	1.773	1.766	1.757	1.746	1.940	1.734
Thermal neutron cross section [2] barns per atom	8.9	0.7	11.2	46	5,500	4,600	46,000	44	1,100	64	166	118	36	108

[1] Promethium, atomic number 61, is an unstable fission product not found in nature. It is not included on this list.
[2] Source: Reference 28.
[3] Symbols: Bcc = body centered cubic; Fcc = face centered cubic; Hcp = hexagonal close packed; Hex = hexagonal; Rhomb = rhombohedral.
[4] Source: Reference 8.

The principal companies in the field market rare-earth compounds, metals, and alloys under a variety of trade names. Those without a trademark name are sold by purity designation. So-called *production chemicals* with lower purities have less exact specifications than those of high-purity materials. Metals and compounds of high purity are usually available in from two to four grades. Purity designations usually refer to the content of the particular rare-earth metal present in the total contained rare-earth metal or of the particular rare-earth oxide in the total contained rare-earth oxide. Analyses of rare-earth ores, metals, and compounds are usually reported as rare-earth oxide, frequently abbreviated to REO.

Cerium, the most abundant element in the group, can be readily separated from the others. The term *didymium* is usually applied or prefixed to the compounds or metals produced from the mixture of rare-earth elements after removal of cerium. Analysis of a typical didymium oxide derived from monazite shows the following percentages of rare-earth oxides: lanthanum, 42.8; neodymium, 30.6; praseodymium, 8.9; samarium, 5.2; gadolinium, 3.3; and other rare-earth and yttrium oxides, 3.2 (*2*). Didymium metal, made from a crude neodymium chloride, is considered by one metal producer as mostly neodymium and praseodymium.

The term *misch metal* is used to denote combinations of the rare-earth elements in metallic form. It may be made from the unseparated elements, usually containing about 50 percent cerium. When it is made from rare-earth elements from which nearly all the cerium has been removed it is called cerium-free misch metal. The metals and misch metal are cast in a variety of forms, such as *ingots* of ¼ and 1 pound; *donuts* of 1, 2, and 5 pounds; *cast pellets* of about 1 ounce each; *extruded pellets* of nearly 1,000 to a pound; and small *granules*, *rods*, *turnings*, and *powder*. Other alloys are made from misch metal and small quantities of aluminum or magnesium. *Ferrocerium* is an alloy of misch metal and iron.

Chemical processing companies, setting their individual requirements for purchase of monazite concentrate, generally want at least 55 percent contained REO. Monazite to be incorporated into the national stockpile must contain 50 percent REO. After leaching with dilute hydrochloric acid, bastnaesite mill concentrate contains about 70 percent REO and after roasting, over 90 percent REO.

TECHNOLOGY

Geochemistry, Mineralogy, and Geology

Geochemical abundance estimates of the rare-earth element content of igneous rocks, which comprise 90 percent of the earth's crust, are derived from data on granitic rocks. These abundance data prove the inapplicability of the prefix "rare" to this group of elements. For example, the three more abundant rare-earth elements—cerium, neodymium, and lanthanum—are collectively greater in abundance than metals such as nickel or copper, and even thulium, the rarest of the rare-earth elements, is more prevalent than silver, gold and platinum combined. In its entirety, the rare-earth element group is greater in abundance than zinc. The rare-earth elements are more abundant in granitic than in basic rocks. Although relatively little research has been conducted on the abundance of rare-earth elements in sedimentary rocks, some data indicate that the content in shales is nearly the same as the average crustal content, but that limestones contain substantially less.

In igneous rocks, rare-earth elements are found in accessory minerals such as monazite, xenotime, and allanite, and sometimes within the crystal lattices of principal rock-forming minerals such as feldspar and biotite.

Monazite has been of principal economic interest because it usually is recovered from sands derived from weathered granitic and pegmatitic rocks. This rare-earth and thorium phosphate mineral contains from about 50 to 70 percent REO, mostly of the cerium subgroup. In some foreign monazite, the thorium oxide content may exceed 10 percent. To date, monazite has been the principal ore mineral for thorium and rare-earth elements. Xenotime, a phosphate mineral analogous to monazite and usually associated with it in small quantities, contains yttrium and yttrium subgroup elements. Apatite, another phosphate mineral, sometimes contains significant quantities of rare-earth elements, notably those of the cerium subgroup, replacing calcium. Of the most common rare-earth silicates, allanite is richer in the cerium subgroup; gadolinite, a beryllium-bearing rare-earth silicate, is richer in the yttrium subgroup. Locally allanite is abundant and occurs in granitic rocks, pegmatites, some metamorphic rocks, and altered marbles and skarns. Some gadolinite has been mined, but it is not a common species and is almost exclusively a mineral of granitic pegmatites. Many early-crystallized minerals such as pyroxenes, amphiboles, and garnets contain heavy rare-earth elements and yttrium replacing bivalent calcium, an element with a similar ionic radius.

Within the past 10 years the mineral bastnaesite, a fluocarbonate with up to about 75 percent REO, mostly of the cerium subgroup, has become an important raw material. The typical occurrence of bastnaesite is in carbonatites, which are carbonate-silicate rocks occurring with and genetically related to complexes of alkalic intrusive igneous rocks. Carbonatites form the rare-earth deposit in the Mountain Pass district, San Bernardino County, Calif., probably the world's largest source of the cerium subgroup elements. Bastnaesite was said to form 5 to 15 percent of much of the Sulphide Queen mass, the largest carbonatite body in the area. A similar association exists in Gunnison County, Colo., where rare-earth and thorium minerals have been recognized in carbonate veins occurring in an alkalic stock.

The multiple oxide minerals containing columbium, tantalum, and titanium, also contain substantial quantities of the rare-earth elements and sometimes significant uranium. These minerals, including euxenite, samarskite, and fergusonite, occur mostly in granite pegmatites and as detrital grains in placers derived from pegmatites and other granitic rocks. Euxenite has been mined in small quantities from placer deposits in the Northwestern United States.

The economic sources of monazite are usually placer and beach sand deposits from which the mineral is recovered as a byproduct of titanium and zirconium mineral mining. In the United States, monazite occurs in the Piedmont province, chiefly in North and South Carolina and Georgia. Crystalline rock belts, the westernmost extending from east central Virginia southwestward into Alabama and the eastern from near Fredericksburg, Va., south-southwestward into North Carolina, are the probable sources of the monazite which has been recovered from southeastern streams and beach placers. Fluviatile placers in streams heading within the Coastal Plain yield monazite and xenotime, as at Aiken, S.C. Littoral deposits are found in present and old beaches. The Pleistocene terraces, some as high as 250 feet above sea level, are in general richer in monazite than are the Recent sites. In Florida, an alluvial deposit near Jacksonville was the only domestic source of monazite in 1963, being a byproduct from dredging for titanium minerals.

Until 1946, Indian deposits, mostly on the southwest coast of Travancore near Chavara and Manavalakurichi, had supplied a great deal of the world's monazite. These beach deposits, containing up to 80 percent heavy minerals, occur in present, barrier, and old elevated inland beaches derived from crystalline granitic and migmatitic basement rocks. The largest

Australian beach sand monazite deposits stretch from northeastern New South Wales north into southeastern Queensland and occur in southwestern Western Australia near Albany. Brazilian deposits consist of the following four types: Elevated beaches, elevated bars, modern beaches, and rare dune deposits formed by wind modification of the other three types (*10*). In general, they were derived by peneplanation of Precambrian rocks during Cretaceous time, subsequent faulting paralleling the coast, formation of sea cliffs, wave undercutting and deposition of concentrated resistates at the bases of the cliffs, enrichment of offshore bars, and finally recent uplift. Deposits in the States of Espirito Santo and Rio de Janeiro are the largest, averaging about 30 percent heavy minerals with some up to 75 percent. Monazite averages 1 to 20 percent of the heavy mineral content in the rich deposit at Comoxatiba in Bahia. A large number of gold river placers in interior Brazil contain monazite.

A unique vein deposit of monazite, until recently the most important source of the mineral, was discovered in 1950 at Van Rhynsdorp, about 200 miles north of Capetown, Republic of South Africa. The vein, which was formed along a shear zone in Precambrian granite, locally contained significant quantities of supergene copper minerals, thereby creating a mineral dressing problem.

Mining and Milling

Dredges, shaking tables, jigs, and Humphreys spirals are some of the equipment used to recover monazite, xenotime, euxenite, and other rare-earth minerals from placers. The bulk concentrate of heavy sands acquired thereby usually contains titanium and zirconium minerals, the main products of the processing of Florida beach sands. Some foreign heavy sands from which monazite is extracted contain cassiterite (tin oxide) as a primary product. Monazite is separated from the other components by various combinations of electromagnetic and electrostatic separation.

In Indian beach sands, leucoxene, an alteration product of ilmenite with magnetic susceptibility close to that of monazite, must be reduced first by roasting at 600° C, a process which does not affect the conductivity of monazite. Flotation also is used for Indian monazite separation and for the vein monazite ore from South Africa which, because of its association with various gangue minerals and sulfides, is not amenable to primary high-tension separation. An improved froth flotation technique uses sodium silicate as a conditioner and sodium or potassium permanganate to improve monazite flotability.

Gangue minerals in the Mountain Pass, Calif., bastnaesite deposit are principally barite, carbonates, and quartz. In a five-stage flotation process ammonium lignin sulfate and heat are used to upgrade an ore averaging 7 to 10 percent REO to a mineral concentrate containing 63 percent REO in the froth. By leaching with 10 percent hydrochloric acid and countercurrent decantation, calcite is removed. The bastnaesite is not dissolved by this treatment and the concentrate is further upgraded to 72 percent REO. Finally, this product can be roasted to remove the carbonate and fluorine ions, resulting in a product with over 90 percent REO.

Concentrate Processing

Industrial chemical processing of monazite concentrates consists initially of digestion in sulfuric acid or caustic soda, subsequent separation of the thorium and other elements, and finally recovery of the rare-earth metals as a group in a pure state. Many variations on standard processing techniques have been devised, some based on sintering and chlorination, but are not applied commercially and are not discussed in this publication.

In the acid process, finely ground concentrate is mixed with concentrated sulfuric acid in externally heated cast iron pots. After roasting under certain conditions of concentration and temperature, the thorium and rare-earth metal portions are dissolved as sulfate in water. Then, in all commonly used methods, the insoluble impurities are separated by filtration. Methods used are proprietary and details can not be given, but in one of the most commonly used acid breakdown schemes thorium pyrophosphate is precipitated from solution by neutralizing any free acid and adding an approximately stoichiometric quantity of sodium pyrophosphate solution. The rare-earth elements are precipitated as an insoluble double sulfate salt by reacting with sodium sulfate solution or as rare-earth oxalate with oxalic acid. Reaction of the double salt with sodium hydroxide provides hydroxide which is treated with hydrochloric acid to form rare-earth chloride. The oxalate can be marketed as such or converted to oxide by ignition. The acid process is adaptable to a wide variety of rare-earth ores, but it has severe corrosion problems and extra processing steps.

In the alkaline process, the monazite concentrate must be finely ground before reacting with a hot concentrated solution of caustic soda in externally heated stainless steel vessels or nickel-clad-steel autoclaves provided with heavy agitators. A one- or two-stage operation is possible,

with the latter reported to require less excess of alkali. In the reaction, the hydroxides of the rare-earth metals and thorium are left undissolved and trisodium phosphate remains in solution to be recovered by crystallization from the filtrate. The hydroxides are washed, dissolved in hydrochloric acid, and subjected to partial neutralization to allow separation of crude thorium hydroxide from the filtrate containing the rare-earth hydroxides. Mixed rare-earth chlorides can be recovered after evaporation in cast iron pans or, with further neutralization of the thorium-free, rare-earth-rich filtrate, a high-grade rare-earth oxide product can be obtained. This method, used by one domestic chemical processor and by plants in France, India, and Brazil, is simpler to use because it removes phosphate and permits separation of pure mixed rare-earth concentrate early in the process, has fewer steps, and makes marketable trisodium phosphate as a byproduct. However, the reagent cost is higher and the process is not amenable to lower grade ores.

Besides the large-scale use of bastnaesite and monazite by standardized industrial processing methods, techniques have been worked out for other, less common rare-earth minerals and sources. For example, in the treatment of the multiple oxide mineral euxenite, which contains yttrium subgroup elements, tantalum, and columbium, chlorination has been used to convert constituents to chlorides. Subsequently, solvent extraction is used to remove tantalum-columbium chloride and hydrometallurgical processing is used to remove rare-earth metals from the chlorination residue (*16*). Other techniques which have been used on euxenite concentrate include digestion with hydrofluoric acid, sulfuric acid, and mixtures of the two, the last reported to be the most effective (*25*).

In Finland rare-earth compounds are extracted from apatite. It has been reported that an apatite deposit on the Kola Peninsula, U.S.S.R., contains large potential reserves of REO and that plants in Russia and in Poland were recovering these oxides during the production of phosphoric acid and fertilizer. The process used includes decomposition with concentrated nitric acid, salting-out of silicic and fluosilicic acids with sodium nitrate, filtering, precipitation of the rare-earth phosphates from the filtrate by partial neutralization with ammonia, dissolution of the rare-earth concentrate in nitric acid, and final purification by oxalate precipitation. A new chlorination procedure for purifying crude rare-earth phosphate was said to eliminate the need for oxalic acid (*3*).

Separation of the Rare Earth Elements

Most commercial rare-earth salts contain individual elements in about the same ratio as in the ore treated. In the separation process, cerium is always the first to be extracted from the mixture. It is oxidized to the tetravalent ceric state and precipitated from solution as a basic ceric salt or crystallized as ceric ammonium nitrate. After the cerium has been removed, the basic rare-earth chlorides are precipitated by adding strong ammonium hydroxide-ammonium chloride solution at 50° C in stages, filtering after each addition. Precipitation is continued until the absorption spectra of the filtrate shows that only lanthanum and ammonium chlorides remain. Lanthanum is the last to precipitate.

Recent advances in the technology of rare-earth element separation suggest that techniques be described under classical and modern methods. The principal classical methods are fractional crystallization, fractional precipitation, and thermal reactions, which include fusion and volatilization. These are the methods used in producing large-scale quantities of the separated salts of lanthanum, cerium, and neodymium. Modern methods include ion-exchange separation and solvent extraction which are used primarily to separate and recover the individual rare-earth elements.

In fractional crystallization, part of a rare-earth mixture is precipitated, usually by evaporating to change the concentration of the salt or by varying the temperature or solvent to affect the solubility of the salt. Fractional precipitation is accomplished by introducing the precipitating agent in small increments allowing certain of the rare-earth compounds to precipitate preferentially to others. Thermal methods have been used to decompose partially rare-earth nitrate salts according to their basicity, which is followed by partial leaching of the salts or the method combined with fractional precipitation (*9*).

Ion-exchange methods consist of elution chromatography and displacement chromatography. In elution chromatography, the driving ion in the eluant is not efficient in displacing the ions sorbed in the column, as the individual rare-earth ions move down the column at different rates. The method is effective only for small quantities obtained for analytical purposes. Displacement chromatography permits the use of a larger fraction of the exchange capacity of a given resin bed and the full driving potential of the eluant. This is the method used commercially to obtain larger quantities of highly purified individual rare-earth elements (*21*).

Ion-exchange equipment consists of columns or tall tanks filled with a resin, such as sulfonated styrene-divinylbenzene copolymer (Amberlite IR–120, Dowex 50, Nalcite HCR, or Permutit Q). Columns used in laboratory work were composed of glass tubing from ½ to 4 inches in diameter by 4 feet high and columns used in commercial operations are from 4 to 60 inches in diameter and up to 20 feet high.

In commercial practice a measured quantity of mixed rare-earth chloride solution is flowed into the top of the column, and the rare-earth cations replace the cations (hydrogen, ammonium, or copper) of the resin; hence, the term ion exchange or, more specifically, cation exchange. In this manner a saturated band of rare-earth elements is formed at the top of the column, and the remaining resin is unaffected. Very little separation occurs in this loading step.

Next, a solution of some negative-ion species which forms a complex ion with the rare-earth elements is passed downflow through the column. Among such solutions, called eluants, are citric acid buffered with ammonium hydroxide to a pH of 2.5 to 3.0 and ammonium citrate with a pH of 5.0 to 8.0. The positive ions in the complexing solution replace the rare-earth ions selectively, so that ions of the most firmly or most strongly complexed element move most rapidly down the column, and the different elements gradually spread into individual bands. As the elution process is continued, each individual rare-earth element can be removed successively at the bottom of the column. The heaviest rare-earth element present is complexed most strongly and moves the fastest, while the next heaviest follows directly behind it. The order of elution then is lutetium, ytterbium, thulium, erbium, holmium, dysprosium, terbium, gadolinium, europium, samarium, neodymium, and praseodymium. If yttrium is in the solution, it is separated after dysprosium and before terbium. Although the bands of individual elements are fairly sharp, there is some overlap where binary mixtures are obtained. The effluent solution is collected in fractions which contain either separated individual elements or binary mixtures of overlapping elements. The separated individual elements are recovered chemically, usually by precipitation with oxalic acid, and the binary mixtures are recycled.

Recently, chelating agents have been used to enhance separation factors, thereby affording greater ease of separation between certain metal ion pairs. Some of these chelating agents are the eluants nitrilotriacetic acid (NTA) used at higher pH's of 7 and 8 to elute elements of the cerium subgroup, ethylenediaminetetraacetic acid (EDTA), and hydroxyethylethylenediaminetriacetic acid (HEDTA). Some afford greater efficiencies under conditions of elevated temperature and are selective with respect to separation of elements within subgroups. Most are necessarily used with the correct special retaining ions. For example, some must be used only with metal ions in the resin from which it is difficult to recover, but others such as HEDTA can be used on hydrogen-state resin beds from which it and water can be recovered and reused. The use of certain expensive eluants, such as ammonium alpha-hydroxyisobutyrate, ammonium thiocyanate, and Zn $(EDTA)^{2-}$, are justified only in elution chromatography.

The outstanding advantage of ion-exchange techniques is the ability to produce very high-purity rare-earth materials. On the other hand, flow rate through the columns must be slow to permit optimum exchange, the equipment is limited in size, and there are limitations on the maximum concentration ranges of currently available complexing agents (*13*).

Solvent Extraction

Although solvent extraction is being used by some segments of the rare-earth industry, details are lacking. The rare-earth elements may be separated from associated impurities as a whole which then is fractionated into subgroups. A typical solvent extraction operation consists of extracting rare-earth ions from an aqueous feed solution, usually of nitric acid, by contacting with an organic solvent such as pure or diluted tributyl phosphate (TBP). The extractability into undiluted TBP from 50 percent nitric acid was shown to increase with increasing atomic number. The rare-earth values are then stripped from the organic phase by a dilute solution, in this case, of hydrogen peroxide. Results of laboratory research indicate the adaptability of solvent extraction to continuous feed operation and the ease of mass transfer from one phase to another. Its primary advantage seems to be in separating mixtures of rare-earth elements into small moderately pure groups or fractions preliminary to final extraction of individual elements by other techniques, such as that of ion exchange.

Metal Reduction

The most common method for preparing cerium and misch metals is by the electrolysis of fused anhydrous rare-earth chloride at about 900° C. Using iron pots as cathodes and graphite rods as anodes, molten metal accumulates at the bottom of the pot. Until recently, rare-

earth elements beyond neodymium—from atomic number 62 onward—had been difficult to prepare electrolytically because of their high melting points, chloride volatility, and high reactivity with cell linings. Other electrolytic methods that have been employed include (1) electrolysis of oxides and fluorides in mixed molten fluoride baths, reported to provide a better metal product with high throughput (*20*); (2) electrolysis of oxides and fluorides in mixed fluoride-chloride baths; (3) electrolysis from molten electrolytes into low-melting-point metals such as zinc and cadmium; and (4) aqueous electrolysis into mercury and amalgam cathodes.

Metallothermic reduction of rare-earth compounds, using lithium, sodium, potassium, and magnesium, also is used to obtain the metals. It has been reported that reduction by calcium has been accomplished in a tantalum crucible or a magnesia-lined steel bomb at 1,300° to 1,500° C (*26*). An alloy of calcium and the rare-earth metal is formed, and the calcium must be removed at a high temperature in high vacuum (*4*). It is difficult to produce high-purity metals by this process, and samarium, europium, and ytterbium cannot be produced as they reduce only to a bivalent compound (*24*).

It has been reported that samarium, europium, and ytterbium can be prepared successfully by reducing their oxides with other rare-earth elements, zirconium, or misch metal (*13*). Purification of rare-earth metals has been accomplished by various methods, chiefly those of distillation and solid-state electrolysis.

By controlling the variables of composition, atmosphere, temperature, and pressure and using a mixed fluoride electrolyte, high-purity cerium and lanthanum have been electrowon by the Bureau on a laboratory scale. Much emphasis has been placed by the Bureau on developing continuous and larger scale electrowining methods, improving metal coalescence, and devising techniques to purify rare-earth metals by solid-state electrolysis. Contamination problems arise from the presence of impurities such as carbon from graphite anodes and from carbon oxide gases. Some of the contamination has been overcome by the use of other, corrosion-resistant materials such as tungsten instead of graphite in cell construction.

USES

The uses of rare-earth elements, as compounds, metals, and alloys, may be grouped by importance into the following categories: (1) In the glass industry; (2) in carbons for arc lighting; (3) in metals and alloys; and (4) in miscellaneous applications.

Rare-earth materials, such as cerium oxide and oxides of the cerium subgroup, are rapid, clean polishing powders used for polishing camera, eyeglass, and instrument lenses, mirrors, plate glass, precision optics, and television tubes. Cerium oxide, added to the melt in small quantities, acts as a glass decolorizer because of its powerful oxidizing action on impurities such as iron. In larger quantities, cerium and neodymium oxides make glass opaque to ultraviolet light, and are used in welders' lenses, better grade sun glasses, and special optical filters. Neodymium, praseodymium, or samarium oxide increase infrared absorption in glass. Some rare-earth oxides, such as that of lanthanum, greatly improve the optical quality of nonsilicate camera lenses having high-refractive indices and sharp definition for light over a large range of colors. A purple glass, using neodymium, absorbs yellow light and is ideal for glassblowers' goggles. In windows exposed to radiation, for example in nuclear reactors, cerium oxide is particularly applicable because of its resistance to color changes caused by alpha-rays. It is used also in color-television tubes, presumably to reduce discoloration. Depending upon the quantities added, neodymium and praseodymium color glass yellow, green, red, or lilac, without changing its index of refraction. The absorptive qualities of glasses containing as little as 1.5 percent cerium oxide appear to afford a great potential use in glass containers to protect perishable food from oxidation, photochemical reactions, or decomposition due to ultraviolet radiation. Research on photochromic materials indicates the probable use of rare-earth ions, such as europium and cerium, in glass that darkens in light of certain wavelengths and loses its hue when the rays are removed.

A yellow ceramic stain uses a praseodymium-zirconium oxide mixture, and some porcelain enamels are opacified by adding cerium oxide.

Rare-earth fluorides and oxides are used in the cores of arc-light carbons in motion picture photography and projectors to provide a light quality close to that of natural sunlight and in searchlights to achieve high light intensity.

An old established use of misch metal is in the production of pyrophoric alloys such as ferrocerium lighter flints. The addition of up to 50 percent iron and small quantities of other metal impurities creates a rare-earth alloy with sparking due to the low ignition temperature and high heat of combustion of cerium. Recently increasing attention has been paid to the application of rare-earth elements in the fields of ferrous and nonferrous metallurgy. In ferrous metallurgy, rare-earth metals and compounds act as deoxidizers, desulfurizers, and

grain refiners. When rare-earth materials are added to certain types of steel under proper conditions, ductility and hot workability is promoted and impact resistance is improved. Misch metal has proved beneficial in improving the ductility of inherently brittle special highly alloyed stainless steels. In the presence of excess quantities of certain harmful elements, such as titanium and antimony, ferrocerium and misch metal were reported to assist in nodularizing cast iron, improving mechanical properties and making possible large castings of high quality.

In nonferrous metallurgy, rare-earth elements, primarily are cerium and misch metal, have been used to retain strength at moderately elevated temperatures in magnesium and aluminum alloys. Some recent uses are in aircraft parts and in flatbed plates in printing equipment. Lanthanum, neodymium, and didymium have been used to promote oxidation resistance and creep resistance in such alloys at elevated temperatures. Attempts have been made to use rare-earth materials in improving properties of high-temperature and refractory alloys such as those containing nickel, chromium, and molybdenum. Cerium added to brass alloys under carefully controlled conditions improves elongation, and addition of small quantities of rare-earth elements reduces the high-temperature oxidation rate of copper without affecting its electrical conductivity.

Important miscellaneous applications include well-established uses and those being developed which show great promise. A large number of chemical reactions including petroleum cracking and chlorine recovery from hydrochloric acid have been accomplished or aided by the use of rare-earth catalysts. Electronic and magnetic applications are in microwave devices such as rare-earth iron garnets and as rare-earth titanates and stannates in ceramic capacitors. Misch metal is used as a "getter" to scavenge the last trace of gas from vacuum tubes. In fluorescent lamp and television tube phosphors, rare-earth elements cerium, gadolinium, and europium act as activators in host materials such as calcium phosphate and halophosphate, calcium aluminate, tungstate, molybdate, and fluoride, and zinc and strontium sulfides. Europium has aroused great interest for its potential use in a superior color television tube phosphor promoting brilliant reds and requiring less voltage. Laser materials include crystals, glass rods, plastic, and liquids doped with rare-earth elements. Crystals of calcium tungstate doped with neodymium and of calcium fluoride doped with didymium emit continuous coherent infrared radiation. Neodymium oxide was used to dope sodium-calcium-silicate glass, europium chelates were used in plastic fiber, and terbium was used to dope a liquid laser material which emitted coherent green light for penetrating ocean depths. Control rods in some nuclear reactors contain rare-earth elements with high-thermal neutron absorption cross sections which have high resistance to radiation damage. The most promising in this application are gadolinium, samarium, and europium. Europium is particularly attractive because of its relatively high cross section and a five-membered chain of absorbing isotopes, permitting slower burnup. Neutron cross sections of the rare-earth elements are given in table 1.

Cerium and neodymium selenides and tellurides are of potential value as semiconductors in thermoelectric devices. Samarium 153 has been used as a radiographic source in a portable X-ray unit. Many other applications of rare-earth elements are noted in the literature, including those in therapeutic and cosmetic preparations, metal soaps, paint driers, refractories, and textile mildewproofing and waterproofing.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Monazite produced from beach sands and river gravel is a product of ilmenite, rutile, and zircon. Other minerals often found associated include gold, staurolite, sillimanite, tourmaline, kyanite, andalusite, spinel, and corundum. Domestically, the heavy-sands rougher concentrate usually contains less than 5 percent monazite; ilmenite and rutile are usually the major constituents and zircon next in quantity. Production from these deposits, therefore, depends primarily on the demand for the titanium minerals. In Malaysia, Indonesia, and Thailand monazite is recovered as a byproduct of alluvial tin mining. Copper was a coproduct in the ore formerly mined for monazite from the vein deposit in the Republic of South Africa.

Bastnaesite ores contain no accessory minerals of great value, although barite probably could be recovered from the Mountain Pass, Calif., deposit.

Processors of rare-earth ores and concentrates have a dfficult problem in byproduct relationship. There has always been a marked difference in demand for different rare-earth elements, yttrium, thorium, columbium, tantalum, and other elements contained in rare-earth minerals. Large stocks of certain rare-earth compounds have been accumulated by industry as a result of processing monazite for thorium formerly required by the AEC.

ALTERNATE MATERIALS

Substitutes are available for many of the applications of the rare-earth elements, and new processing techniques may be harmful to budding uses.

The rare-earth oxides, arsenic, and selenium are partly interchangeable for decolorizing glass. However, rare-earth compounds have no substitutes in the production of special glasses for absorption of the ultraviolet or yellow portions of the light spectrum. Rouge and possibly some alumina abrasive compounds are cheaper and can replace cerium and mixed rare-earth oxides for optical polishing but are less effective and not as clean to work with. The potential use of rare-earth elements in curtain windows (variable transmissibility glass) may be affected adversely by concurrent research on cheaper substitutes such as silver and certain organics. The new Pilkington float process, by which flat glass is deposited while molten on a bed of molten tin, may limit one of the most promising markets for cerium and rare-earth oxide abrasives.

In carbon-arc electrodes, rare-earth compounds are far superior to any other material. Iron and calcium fluorides were used by Germany in World War II, but the light from these materials is about 30 percent less intense than that from rare-earth fluorides. Furthermore, such substitute electrodes are unsatisfactory for color photography because the light emission does not have the proper color balance.

Lighter flints have been made of zirconium-impregnated lead, but they are more expensive and not as satisfactory. Additions of magnesium-rich nickel alloy and ferrosilicon are used to produce ductile nodular iron. In the unlikely absence of certain "subversive" elements, the magnesium treatment to produce ductile iron is more efficient and less expensive than that using cerium.

In thermal neutron absorbers for control rods boron is cheaper than rare-earth compounds and creates no secondary alpha-radiation for which additional shielding must be provided. Hafnium rod is less expensive than stainless-steel cermets containing europium oxide, but the europium oxide is said to be equivalent to massive hafnium at 20 volume-percent concentration.

RESOURCES AND RESERVES

Domestic rare-earth mineral deposits have been reported in 31 States (*19*). The recorded domestic occurrences of monazite are largely in recent southeastern beach placers, that is, in Florida where some production has taken place recently, and as fossil placers, largely in Idaho and Montana. Monazite resources have been depleted very little by production, and exploration in the Southeastern States indicates that beach deposits on the Sea Islands contain substantially more monazite than previously estimated. For example, beach deposits on one island alone were estimated to contain over 100,000 tons of monazite or about 60,000 tons of contained rare-earth oxides (*17*). Despite rising production, the large deposit of bastnaesite at Mountain Pass, San Bernardino County, Calif., still contains an estimated 5 million tons of rare-earth oxides, probably 80 to 90 percent of the U.S. total reserve.

There are extensive monazite placer deposits in India, Brazil, and Australia. Deposits along the southwestern coast of India are estimated to contain over 1.4 million tons of monazite. Other deposits are known on the eastern coast, but reserve figures are not available because of lack of data due to insufficient exploration. The reserve estimate also excludes large monazite placer deposits discovered in 1956–57 in Bihar and West Bengal. Some of these deposits were reported to contain about 35,000 tons of monazite per square mile.

In Brazil, monazite beach deposits extend along the coasts of the States of Espirito Santo, Bahia, and Rio de Janeiro. The total monazite reserve, including these beach deposits and extensive fluvial placer deposits, was estimated as over 300,000 tons (*1*).

Australian monazite is largely a byproduct of beach sand mining for ilmenite in the southwestern part of Western Australia. Other production in eastern Australia is the result of mining of beach sands for rutile in the contiguous coastal areas of southeastern Queensland and northeastern New South Wales. Original estimates, some of which were not considered too accurate, placed the eastern Australian reserves at nearly 50,000 tons of monazite (*6*). The average thoria content of the monazite was reported to be 6.6 percent (*23*). Using this figure as a base and applying it to Canadian figures on total thoria resources for Australia, it was estimated that beach sands contain approximately 800,000 tons of monazite (*7*).

In Africa, measured and indicated reserves in Malagasy Republic total about 130,000 tons of monazite found in beach sands in the southeastern part of the country (*18*). The vein monazite deposit in the Republic of South Africa is stated to contain reserves large enough to sustain 2 or 3 years of mine operation if there was a demand. Malawi has recoverable reserves of 13,000 tons monazite and, in North Africa, huge deposits of heavy minerals estimated to contain about 200,000 tons of monazite occur in

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Egypt in the Nile delta. In Asia, placer deposits of lesser size are known in Malaysia and Indonesia, where monazite is a byproduct of tin mining, Ceylon, and the Republic of Korea. In South America, outside of Brazil, beach sands containing monazite are known in Uruguay and other deposits were recently discovered in Cordoba Province, Argentina.

Other sources of rare-earth materials, largely as byproducts, are available if needed. A typical example is the commercial production of rare-earth oxides from apatite, recently undertaken in Finland. In the United States substantial quantities of rare-earth-bearing apatite are known in tailings piles resulting from magnetic iron ore processing.

SOURCES OF STATISTICAL INFORMATION

The Bureau obtains annual data on production and shipments of rare-earth ores and concentrates by domestic producers and on production and consumption of rare-earth chemicals and their use by consumers. Mineral production is covered completely by the canvass. Complete information on consumption and usage is difficult to obtain because of confidentiality restrictions imposed by several major companies. From 1946 to July 1, 1955, thorium production was under security classification by AEC, and statistics on monazite could not be released. Prior to 1961 import data on monazite were not available because of agreements with foreign governments.

PRODUCTION, CONSUMPTION, AND TRADE

Through 1963, the world production of monazite has been about 270,000 short tons, of which almost 37 percent has been in Brazil, almost 24 percent in India, over 22 percent in the Republic of South Africa since 1952, about 6.5 percent in the United States, 5 percent in Australia, 2 percent in Malaysia (Federation of Malaya), and the rest in Indonesia, Ceylon, Korea, Thailand, the Congo (Leopoldville), Malagasy Republic, and Nigeria.

During World War II and until 1955 production figures were classified. Recent monazite data disclosing individual company operations cannot be divulged. Known disclosable domestic production of monazite concentrate from 1948 through 1963 was nearly 9,000 tons, but publishable data also showed shipments totaling over 3,500 tons. From 1960 to 1963 the known domestic monazite production by the one company processing Florida beach sands primarily for titanium minerals cannot be disclosed, but it has dropped significantly from the annual totals of the companies that produced in the 1950's. Similarly, figures on bastnaesite production continuing in California cannot be given. Stoppage of monazite export, because of its thorium content, by India and Brazil had been a factor in the resurrection of the domestic industry, but the close of the AEC thorium buying program, the availability of large tonnages of monazite from South Africa, the huge reserves of California bastnaesite, increased imports from other foreign producers, and high operating costs have created a prolonged lull in the domestic mining industry. The South African source was closed down in 1963 and henceforth domestic demand apparently will be more dependent upon Australian and other larger foreign producers as well as upon domestic bastnaesite.

Following the close of the AEC thorium buying program no monazite was imported by U.S. firms in 1960. From 1961 through 1963, however, chemical processors indicated they acquired nearly 17,000 tons of monazite of which 75 percent came from the Republic of South Africa, 15 percent from Australia, and the rest from Malaysia and Ceylon.

The apparent industrial consumption of REO in compounds, metals, and alloys in 1963 was about 2,350 short tons. From 1960 through 1963 average apparent consumption of REO, as derived from shipments, was about 2,000 tons per year. This was processed mostly from monazite, of which over 17,500 tons was consumed, and from bastnaesite. Production of bastnaesite concentrate dropped 25 percent from 1960 to 1963, but the grade increased. Shipments of bastnaesite concentrate in 1963 were over 1,200 percent greater than they were in 1960.

The quantity of imports of cerium compounds, metals, and alloys has decreased markedly since 1957, but the average unit cost (determinable by comparing ratio of weight to value) rose significantly in 1958 and has remained high. In 1963, a total of 22,835 pounds of compounds, metals, and alloys (including ferrocerium) worth $57,273 was imported. In the same period 168,712 pounds of cerium ore, metals, and alloys (including lighter flints) valued at $223,781 were exported.

Tariff changes on processed rare-earth materials became effective in 1963. Cerium metal was divided into two classes of rare-earth alloys, one consisting wholly or almost wholly of rare-earth metals (misch metal). Cerium alloy including ferrocerium became ferrocerium and other pyrophoric alloys. A new category was adopted for higher purity rare-earth metals.

STRATEGIC CONSIDERATIONS

Even if imports of monazite concentrate were halted, sufficient domestic supplies of rare-earth elements would be available from the California bastnaesite deposit. Any present requirements for light subgroup metals could be met from the mining and milling capacity of the Molybdenum Corp. of America plant at Mountain Pass.

From 1946 to 1950, when India, Australia, and Brazil decided to nationalize their production of monazite for their own use, the strategic situation for the rare-earth metals appeared critical, and they were placed on the Group 1 stockpiling list. For a time, many rare-earth compounds were placed under closed or restrictive export controls. Some of the first production of bastnaesite from Mountain Pass, Calif., was purchased for the stockpile under contract with Molybdenum Corp.

Although monazite stocks held by companies are large at this time, the closing of the South African vein monazite deposit will force the industry to depend upon byproduct monazite from Australia and Malaysia. There is a larger excess of rare-earth oxide in material held in the strategic stockpile, as shown by the new lower stockpile objective—3,000 short tons of REO—announced by the Office of Emergency Planning in the spring of 1964.

On June 30, 1964, government inventories totaled 15,800 tons, of which 10,000 tons was in the national (strategic) stockpile, and 5,800 tons was in the supplemental stockpile.

GOVERNMENT PROGRAMS

The Office of Minerals Exploration (OME) provides financial assistance for exploration for monazite or other rare-earth minerals to qualified applicants.

The accelerated tax amortization program under the Defense Production Act was closed in August 1955 after $4,771,000 had been granted to processors and producers. No other programs are in effect or under consideration.

PRICES

For about a decade the nominal prices on imported monazite have been based on its rare-earth oxide and thorium oxide content. During this period the only changes in price have been on the 55-percent massive variety, which rose from 13 cents to 14 cents per pound in 1958, and for the 55-percent sand variety, which in mid-1960 changed from a rigid 15 cents to a range of 10 to 15 cents per pound. The monazite sands of 66 and 68 percent grades have remained at 18 cents and 20 cents per pound, respectively. Known prices of monazite produced and exported from six countries since 1960 ranged from 3 to 12 cents per pound of monazite concentrate. Company confidentiality prevents divulgence of prices paid for domestic monazite mined by a limited number of companies since 1959. A similar restriction exists on disclosure of the price of bastnaesite concentrate mined by one company in California.

Prices listed by one company on intermediate lot sizes of most commercial rare-earth compounds, referred to as production chemicals, were increased in 1963 over those in effect in 1960. For example, in 1963 and 1964 the price for rare-earth chloride in 50- to 99-pound lots was about 60 percent greater than that in 1960, and that for rare-earth oxide in the same size lots was about 35 percent more. Larger size lots of high-purity compounds were available from all companies. In many instances prices of high-purity compounds remained stable, but prices were increased moderately on others and substantially on several compounds of the scarcer rare-earth elements. In 1963, one company lowered prices on most of its high-purity oxides. Another company reduced prices on oxides twice in 1963, in some cases about 20 percent. Prices of other rare-earth salts are usually based on percentages of oxide prices.

Prices for misch metal in 1963 ranged between $2.60 and $3.50 per pound, depending upon grade, the quantity ordered, and whether it was in the form of ingots, donuts, pellets, or extruded pellets. Larger size lots of high-purity metals have become available recently. Quoted prices for small pound lots of high-purity metals from a major producer ranged from $123 per pound for cerium to $4,250 per pound for lutetium. Metal prices, generally on slightly smaller lots, from another company were increased slightly in early 1964 but ranged from $73 to slightly over $5,600 per pound. This company did not quote a pound price for lutetium metal. A third company cut prices on some metals by almost half in a period of 2 years and twice in 1963 reduced prices on some metals by several percent to over 25 percent.

TAXES

Rare-earth minerals, with the exception of monazite, are eligible for 15 percent depletion allowance on gross incomes from mining. Domestic monazite, because it is an ore mineral of thorium, is eligible for a 23-percent depletion allowance. A depletion of 15 percent is allowed on foreign production of monazite and other rare-earth minerals.

RESEARCH

Industry, educational and research institutions, private foundations, a number of Federal agencies, and foreign governments have spent and are continuing to spend large amounts of money on rare-earth research. The Lindsay Light Co., now the Rare Earth Division of American Potash & Chemical Corp., was an early industrial pioneer in developing uses for rare-earth materials. The advent of nuclear technology aroused increased interest in these elements, of which the AEC had a large share. Institutions working with or under the Commission are the Ames Laboratory at Iowa State University, Ames, Iowa, where ion-exchange techniques were developed (*26*, *27*) and distillation of metals has been investigated; Oak Ridge National Laboratory where effective solvent extraction methods have been devised; Los Alamos Scientific Laboratory where aqueous electrolytic extraction and phase studies have been investigated; and Argonne National Laboratory, where physical properties of metals have been determined. Other organizations working for the AEC on rare-earth projects include the General Electric Co. which has studied rare-earth compounds in neutron absorbers, and Battelle Memorial Institute, where semiconductor research has been underway. Sponsored by the Air Force Office of Scientific Research, scientists at RCA have investigated the use of rare-earth materials in lasers, and investigators at the University of Denver have made phase studies and determined thermochemical properties. Investigators at the Bureau of Ships, Department of the Navy, have conducted research on thermoelectric materials and the Bureau has sponsored investigations by Westinghouse Electric Corp. on semiconductors. The Office of Naval Research has helped finance laser research by General Telephone & Electronics Laboratories, Inc., and, with the National Science Foundation, has financed research by universities on the physical properties of the rare-earth elements. Scientists at the National Bureau of Standards have investigated physical properties and phase phenomena. Molybdenum Corp. of America and Pennsylvania State University have cooperated on a product-and-use study on bastnaesite.

All aspects of rare-earth research were discussed at four conferences held in the United States since the fall of 1960. At the most recent meeting, sponsored by Arizona State University and the U.S. Air Force Office of Scientific Research, there was increased emphasis on utilization of rare-earth materials in laser research and the gathering included a number of distinguished foreign contributors. New trends in the investigation and application of rare-earth elements were reported in a conference held in Moscow in March 1963 in which wider use of rare-earth elements in research and industry was recommended.

From 1948 to 1952, the Bureau of Mines cooperated with the AEC and the Geological Survey in extensive investigations of monazite resources (*5*, *11*, *14*). More recently the Bureau has compiled information on rare-earth metals and thorium deposits in several Western States (*12*), and currently studies are underway to evaluate tailings piles from magnetite iron ore processing as a potential source of rare-earth elements. The Bureau's metallurgical program has included intensive research on analytical procedures, thermodynamic studies, extraction from ores and concentrates, separation of the individual rare-earth elements from one another, their reduction to metals, and physical metallurgy of the metals and their alloys.

OUTLOOK

Rare-earth metals and compounds are expected to be consumed on a slightly increasing scale in the next few years in such conventional uses as metal and glass manufacturing and continued to be consumed at the same rate in the production of carbon-arc electrodes. Misch metal and newly developed rare-earth silicides will be used to deoxidize, reduce grain growth, and improve castability in certain types of steel and promote graphite nodularization in ductile cast iron. Consumption by the glass industry will be mostly as oxide polishing compounds used largely for grinding prescription eyeglasses and instrument lenses, as well as in the manufacture of mirrors. Fluorides and oxides will continue to be used in the cores of arc-light carbons.

The large increases in the consumption of rare-earth compounds, recently believed imminent because of anticipated greater long-range applications or expansions, probably will not develop because of new production methods or alternate materials. Large-scale flat glass polishing using rare-earth oxides probably will not develop as much as hoped for because of the recent development of the float glass process that produces plate glass that does not require the extensive polishing of glass produced by the old process. Furthermore, rare-earth chloride usage in fixed-bed petroleum cracking catalysts may not become as large a consumption factor as believed previously because of competition from the large-scale use of other types of fluid-bed cracking catalysts.

The long-range outlook, then, is for a steady but not explosive growth in consumption with any acceleration being contributed by uses now in their infancy or in the process of development. Many of these newer or potential uses will require separated extremely pure rare-earth compounds or metals. This is true especially in certain magnetic materials and for rare-earth compounds used in laser and television phosphor applications. A type of glass window, able to transmit and absorb sunlight rapidly, may depend upon absorption bands characteristic of rare-earth additives. Certain rare-earth sulfides may be useful in thermoelectric materials at elevated temperatures. Because of their superior neutron-absorption qualities, some rare-earth elements will be used increasingly in reactor control rods in commercial nuclear powerplants.

One of the least abundant of the rare-earth elements, europium, shows great possibilities as a television phosphor, laser, and control-rod material. Increased processing of rare-earth ores or reprocessing of residues might be required to meet a greater demand for this element. The likelihood exists that, by the last decades of this century, the processing of ores for the extraction of thorium required to generate nuclear energy also will provide by-product rare-earth metals. Other rare-earth elements may be extracted, as now done commercially in Finland, from apatite, a phosphate mineral often associated with magnetic iron ores and forming substantial parts of extensive mine tailings piles.

Generally, advances in technology will result in overall decreases in processing and refining costs. Prices for europium or other metals in great demand, however, probably will rise to offset the processing and storage costs of the excess rare-earth compounds.

PROBLEMS

Resource problems are created by the complex relationship of the rare-earth elements rather than by their scarcity. The occurrence of the suite of rare-earth elements in rare-earth deposits and as byproducts of varied significance in other ore deposits normally creates an inherent instability in rare-earth mineral supply economics. This problem is intensified from time to time by the accumulation of surplus rare-earth materials as byproducts of other commodities or of particular rare-earth elements in greater demand. The current situation is one of oversupply for most of the rare-earth elements; the main problem being to find markets. This problem probably will become more acute as the need for europium or other scarce rare-earth metals may lead to creation of excess quantities of the more abundant rare-earth elements. There probably will be the loss of a significant portion of the polishing compounds market due to the development of the float glass process. Producers often are handicapped by scanty knowledge of the extent and nature of some rare-earth resources, partly because certain rare-earth minerals are difficult to recognize. In addition to the influence of normal economic factors, instability also results from political and strategic policies in this and in foreign countries on exploitation of monazite because of the potential nuclear energy applications of its thorium content.

Limited knowledge of some of the unusual properties of extremely pure rare-earth metals and compounds continues to hamper development of new uses upon which the rare-earth industry depends for much of its expansion. The need for concentrated utilization research on mixed and pure materials probably is greater than scattered or unorganized basic research on physical and chemical properties of metals and compounds.

The difficulty of recognizing rare-earth minerals in the field handicaps the search for new deposits. Precise laboratory analyses for individual elements in rare-earth metals and compounds are difficult because of the low order of magnitude of impurities permitted for most new uses. This usually prevents use of ordinary chemical analyses necessitating methods involving emission and X-ray spectrography, neutron activation and atomic absorption, and advanced laser spectrography.

Typical placer mining problems are common to many rare-earth deposits. Sampling procedures are sometimes unreliable, mineral dressing methods (particularly in separation of fine-grained material) need improvement, and tailing disposal, land reclamation, and stream pollution create special problems of growing intensity. Improved quarrying or underground mining, crushing, and benefication methods are needed for disseminated rare-earth mineral deposits.

Technologic problems exist in all stages of rare-earth mineral processing. Mineral dressing and extractive processes used for rare-earth ores and other source materials are complex and time consuming. Natural raw materials vary in composition; similar materials from different sources vary in amenability to concentration and recovery. The separation of individual rare-earth elements from one another is difficult because of their chemical similarity. Clean-cut separation of elements of adjacent atomic numbers is particularly difficult, and it often

requires numerous processing stages or large quantities of expensive reactants to obtain pure compounds with reasonably high recovery. Problems encountered in metal production are those of incomplete reduction and the difficulty of collecting homogeneous metal nodules, the need for better construction materials for processing equipment to minimize contamination, the selection and development of suitable electrolytes, the lack of rapid continuous metal production processes, and the removal of certain impurities retained after ordinary refinement.

Distances between sources of supply and markets are usually large, with resulting high freight costs.

Statistical data accumulation and dissemination continue to be hampered by the restrictions companies place on the publication of production and consumption figures. Sometimes information on new uses is not readily available.

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[3] Titles enclosed in parentheses are translations from the language in which the item was originally published.

RHENIUM

By Richard F. Stevens, Jr.[1]

ALTHOUGH the existence of rhenium was predicted over 100 years ago, it was not isolated until 1925. Since that time, rhenium has been found in minute quantities in many minerals. It is obtained commercially only from the molybdenite concentrate of porphyry copper ores. Germany supplied the world's rhenium requirements until World War II. When U.S. imports from Germany were halted, domestic sources of rhenium were developed from the flue dust obtained during the roasting of Arizona molybdenite.

The University of Tennessee, the first domestic rhenium producer, roasted the molybdenite and processed the flue dust. Kennecott Copper Corp. later found rhenium in the molybdenite recovered from southwestern copper ores. During the roasting of molybdenite to form molybdenum oxide the rhenium oxide volatilizes. Chase Brass & Copper Co., Inc., a subsidiary of Kennecott Copper Corp., developed a method to recover rhenium from the flue gasses. In 1954, Chase began recovering rhenium and producing rod, wire, strip, foil, and other shapes of pure rhenium.

Prior to World War II the main use of rhenium was in thermocouples and pen points. However, in 1963, approximately 80 percent of the rhenium consumed was used in tungsten and molybdenum alloys. A minor amount of rhenium is used in electronics, thermocouples, electrical contacts, catalysts, and coatings. Research is being conducted to seek commercial applications of pure rhenium. Because of its high melting point rhenium is being studied for use in high-temperature and corrosion-resistant alloys.

In 1963 the domestic consumption of rhenium metal reported to the Buerau of Mines by five major consumers was almost 500 pounds which was believed to represent approximately 85 percent of the total domestic consumption. It is expected that the consumption will continue to increase significantly. Domestic resources of rhenium from molybdenite sources are estimated to be from 200 to 250 short tons.

In 1963 rhenium metal powder sold for $650 per pound up to 1 pound and prices decreased to $580 per pound for lots of 20 or more pounds. Wire, strip, foil, and other shapes are available at approximately $750 to $1,200 per pound. The principal problem associated with rhenium is its limited supply.

BACKGROUND

When the first periodic table of elements was published by Mendeleev in 1860 provisional names were given to several unknown and undiscovered elements; element 75 was named dvimanganese. In 1925 chemists in Germany, Great Britain, and Czechoslovakia (*3*) [2] almost simultaneously claimed the isolation of element 75, and Dr. Walter Noddack, Ida Tache, and O. Berg, of Germany were credited with discovering rhenium, naming it after the river Rhine. They identified rhenium in 5 of 30 complex mineral samples and produced 50 milligrams of residue containing 5 percent rhenium from a kilogram of columbite. In 1929 the discoverers produced 1 gram of rhenium from 660 kilograms of Norwegian molybdenite.

Before World War II, Germany supplied the world with rhenium. Potassium perrhenate was produced commercially in the middle 1930's from potash residues (brown salts), now exhausted, by Vereinigte Kaliwerke in Aschersleben, East Germany. Degussa processed the perrhenate and it has been reported that 200 kilograms of rhenium was extracted annually. Another source was the rhenium-bearing residues and dusts from the Mansfeld coppersmelter at Eisleben, East Germany.

[1] Commodity specialist.
[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

In 1942 Professors A. D. Malaven and J. A. Bacon, at the University of Tennessee, found a source of rhenium in molybdenite roaster flue dusts from the Miami Copper Co. smelter, Miami, Ariz., and developed a method for recovering the rhenium from this source. Subsequently, the University became the first domestic producer of rhenium. Kennecott Copper Corp. later found rhenium in molybdenite in its southwestern low-grade copper ores and began recovering the element in 1954 and shipping it in 1955.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Rhenium is produced in the United States by the chemistry department, University of Tennessee, Knoxville, Tenn., and by Chase Brass & Copper Co., a subsidiary of Kennecott Copper Corp., Waterbury, Conn.

DEFINITION OF TERMS AND GRADES

Rhenium melts at 3,180° C, has a density of 21 grams per cubic centimeter, and a modulus of elasticity of 67×10^6 pounds per square inch (*4, 5, 6*). In elemental form, only tungsten and carbon have higher melting points; only platinum, iridium, and osmium are denser, and only osmium and iridium have a higher modules of elasticity. The element retains its ductility after heating at high temperatures. The ultimate tensile strength of annealed rhenium sheet is about 168,000 pounds per square inch, and that for cold-rolled rhenium sheet reduced 30 percent is 322,000 pounds per square inch. The element has hexagonal close-packed crystal structure, and its elevated-temperature strength is higher than either tungsten or tantalum, which have body-centered cubic crystal structures. Rhenium oxidizes in air, and when heated to 1,000° C oxidizes at about the same rate as tungsten. Rhenium is the most refractory of the metals that can be electrodeposited from aqueous solution. The element resists corrosion by hydrochloric and hydrofluoric acid, is little affected by cold sulfuric acid, but is readily dissolved in nitric acid. Rhenium has valences −1, 1, 2, 3, 4, 5, 6, and 7.

Rhenium alloys with chromium, cobalt, columbium, iridium, iron, gold, mercury, molybdenum, palladium, platinum, nickel, osmium, rhodium, tantalum, tungsten, and vanadium but not with carbon, copper, silver, tin, or zinc. Some rhenium-molybdenum alloys have high-temperature strength and very high ductility. A 50-percent rhenium-molybdenum alloy has a melting point of more than 2,500° C and can be cold-rolled to more than 90 percent reduction without failure. At 800° C, the hardness of this alloy is about 200 Vickers Hardness Number (VHN) in annealed condition and 350 VHN in worked condition. Tungsten and molybdenum have hardnesses of 70 and 80 VHN, respectively. Tungsten alloys containing 30 percent rhenium and molybdenum alloys containing 50 percent rhenium are considerably more ductile than unalloyed tungsten or molybdenum.

Rhenium forms compounds with metals such as arsenic, germanium, selenium, silicon, titanium, zirconium, and with non-metals such as oxygen, phosphorus, sulfur, and halogens. Organic compounds containing rhenium also have been produced.

TECHNOLOGY

Geology

The average concentration of rhenium in the earth's crust is estimated at one part per billion, or about one fifteen-thousandths as much as molybdenum, the element with which it commonly occurs (*5*). It has been found in minute quantities in many minerals including alvite, chalcocite, chalcopyrite, columbite, gadolinite, molybdenite, orangite, pyrolusite, rutile, tantalite, thortveitite, wulfenite, and in rare-earth minerals and in ores of copper, manganese, molybdenum, platinum, uranium, and potash.

Metallurgy

Processes have been developed to extract rhenium from platinum ores, molybdenite-bearing flue dusts and gases, pig molybdenum, and residues from potash operations. During the milling of copper ores of Miami Copper Co., Miami, Ariz., and southwestern low-grade copper ores of Kennecott Copper Corps., rhenium-bearing molybdenite concentrate is produced as a byproduct. When the concentrate is roasted, rhenium oxide is volatilized, and it is recovered from flue gas and dust.

At the University of Tennessee, flue dust containing rhenium oxides and unconverted molybdenum sulfide, is leached with water and filtered. The filtrate, containing soluble rhenium heptoxide, is treated with solid potassium chloride and crude potassium perrhenate is precipitated. This precipitate is reduced to rhenium metal with hydrogen at 300° C under 3,000 pounds per square inch in a silver-lined bomb.

Kennecott Copper Corp. uses the following rhenium recovery process (*13*). Gas from the

roasting of molybdenite concentrate is cleaned of dust particles and scrubbed with water to dissolve the rhenium oxide. The solution is clarified, conditioned, and passed through ion-exchange equipment. Processing is continued until high-purity ammonium perrhenate is produced. To produce metal powder (*2*), finely ground, high-purity ammonium perrhenate is placed in 8-inch-long molybdenum containers (boats) to a depth of about five-eighths of an inch. The boats are loaded into an externally heated furnace of stainless steel pipe 2 inches in diameter by 12 feet long, and purified dry hydrogen is passed through the pipe to reduce the compound to rhenium powder.

Powder-metallurgy techniques are used to prepare metal shapes. Powdered metal compacts are pressed at 25 to 30 tons per square inch, vacuum presintered at 1,200° C for 2 hours, sintered with hydrogen at 2,850° C and shaped by alternate cold working and annealing. Products are rod, wire, strip, foil, and disks.

USES

Before World War II, rhenium was used commercially in pen points and thermocouples. Its major use now is as an alloying addition to tungsten and molybdenum. Tungsten-rhenium thermocouple elements have been developed which can measure and control temperatures up to 2,500° C. Rhenium also is used in other kinds of thermocouples; in filaments for mass spectrographs for analyzing gases; and in filaments for ion gages for measuring high vacuum (*2, 4, 10*). Most rhenium being produced in the United States is used in research on the properties and potential applications of the metal and its alloys. Some promising uses are as vacuum tube filaments, cathodes, and cathode supports and heaters; as lamp filaments; and in electrical contacts. Other uses developed for rhenium include filler rod for welding molybdenum and tungsten; heat-, wear-, and corrosion-resistant alloys; plating; and as a catalyst.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Rhenium is a byproduct of molybdenite derived from copper sulfide ores. Deposits mined principally for molybdenite usually contain little or no rhenium.

ALTERNATE MATERIALS

Technetium, which is recovered from the waste fission products of nuclear reactors and consequently has a potentially large supply, may be substituted for rhenium in alloying applications. Since rhenium and technetium have similar properties and structure they form the same type of alloys. The slight beta particle radioactivity of technetium is shielded by alloying. The use of technetium will be dependent upon the availability of waste isotope reprocessing facilities and the price of separating technetium from accompanying radioactive fission products.

Because technetium is radioactive, it is not a suitable substitute for rhenium in all of its uses.

RESOURCES

At present the only commercial source of rhenium is as a byproduct of molybdenite which itself is a byproduct of low-grade porphyry copper ores. In the United States the reserve of rhenium in copper ores is estimated at 200 to 250 short tons. Other countries which have copper ore deposits containing byproduct molybdenite include: Canada, Chile, Peru, and Mexico. Although rhenium may occur in these deposits, no production has been reported. The free world reserve of rhenium from byproduct molybdenite is estimated at about 400 to 600 short tons. At 50- to 80-percent recovery about 6 tons of rhenium could be produced annually if all presently recovered domestic byproduct molybdenite was treated. Additional rhenium resources may become available from other molybdenum, uranium, manganese, tungsten, zirconium, columbium, tantalum, and gadolinium ores.

Recovery of rhenium from reserves in molybdenum or porphyry copper deposits has been reported in Europe and the U.S.S.R.

PRODUCTION AND CONSUMPTION

The current consumption of rhenium in the United States has been estimated at 500 pounds per year. The potential production of rhenium from molybdenite sources in the United States has been estimated at 6 tons per year.

Rhenium production and consumption in Europe and U.S.S.R. are believed to be small.

TARIFF

Rhenium ore and concentrate enters the United States duty free. Under the "Tariff Schedules of the United States, Annotated (1963)," the duty on unwrought rhenium metal or compounds is 10.5 percent, ad valorem, and the duty on wrought rhenium metal is 18 percent, ad valorem. The corresponding Statutory Rates of Duty are 25 percent, ad valorem, and 45 percent, ad valorem.

PRICE

Rhenium powder was priced at $14 per gram in 1942, $10 in 1943, $6.50 in 1944, and $3.25 per gram in 1946. In 1963, Chase Brass & Copper Corp. quoted rhenium powder, Grade I, at $650 per pound ($1.43 per gram) in ½-pound lots. Prices for rhenium rod having diameters ranging from 0.2 to 0.025 inch were quoted at $900 to $1,260 per pound, respectively, and for rhenium strip having thicknesses ranging from 0.06 to 0.001 inch at $815 to $1,580 per pound, respectively. Rhenium sintered bar was quoted at $800 per pound up to 1 pound, $775 per pound for quantities between 1 and 5 pounds, and $750 per pound for quantities over 5 pounds. The base quotations for rhenium wire ranged from $65 per foot for wire of 0.100 inch diameter to $2.65 per foot for wire of 0.010 inch diameter.

RESEARCH

During World War II the University of Tennessee developed and patented a process to extract rhenium from molybdenum roaster flue dust. Since then, the University has occasionally announced research on preparation, isolation, physical properties, and uses of rhenium and its salts.

Kennecott Copper Corp. developed methods to extract rhenium incidental to the production of molybdenum oxide (*13*), and also developed methods to shape the metal (*2*).

Important contributions to rhenium technology have been made in the past few years as a result of work conducted by Battelle Memorial Institute and the National Aeronautics and Space Administration (NASA). Rhenium research, conducted primarily on alloying investigations, has been sponsored by the U.S. Air Force, Navy, and Atomic Energy Commission (AEC) (*7*).

The Buerau of Mines has conducted research on rhenium and published reports on its investigations (*1*, *8–9*, *12*). Current research by the Bureau on rhenium and tungsten-rhenium alloys is being conducted in cooperation with the AEC and Chase Brass & Copper Co. Research on vapor deposition of rhenium and tungsten-rhenium combinations from halide gasses is also being conducted by the Bureau.

OUTLOOK

The outlook for rhenium is for continued and increasing usage. The major consumption of rhenium will be as an alloying element with tungsten and molybdenum where rhenium additions lower the ductile-brittle transformation temperatures of the alloys and allow fabrication to be conducted at room temperature. Pure rhenium metal will continue to be used in electrical contacts, thermocouples, catalysts, and coatings. However, because of its high price and short supply the use of rhenium in these applications will represent a minor part of the total rhenium consumption.

Although the demand for rhenium as an alloying element will increase, its use will be limited by the limited supply. Development of a larger supply of rhenium would cause the applications to increase and the price to decrease. It appears unlikely that such a supply source will be found.

Unless rhenium recovery techniques are utilized by all processors of molybdenite obtained from porphyry copper ores, all the available rhenium will not be recovered.

PROBLEMS

The principal rhenium problems are its limited supply and high cost. As new sources of supply are found the price will decrease. Although the potential supply of rhenium is adequate for the immediate future, there is a current resource problem caused by the fact that approximately 50 percent of the rhenium occurring with molybdenum is not being recovered.

Although there is a need for continued research on rhenium and its alloys and compounds, to obtain more complete knowledge of these materials, the major need is for more intensive and extensive resource exploration to discover new sources of rhenium and for more research on methods of extracting rhenium from presently known submarginal resources. A partial solution to the problem of short supply might be that proposed by the Materials Advisory Board in its report (*6*), which recommended that rhenium be considered a strategic material and be purchased and stockpiled by the U.S. Government.

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RUBIDIUM

By Donald E. Eilertsen [1]

RUBIDIUM, a highly reactive metal with air or water, was discovered in 1861. Numerous firms have processed raw materials to rubidium primary products during the last few years, but most of these operations discontinued. Currently most production of rubidium and its compounds is from accumulated stocks of alkali carbonates from operations that formerly processed lepidolite to lithium compounds. Some rubidium output has come from processing pollucite for cesium. Outputs of rubidium and its compounds are small but trends are upward. Very little is known about the resources of rubidium in commercial concentrations even though the element is more abundant than zinc in the earth's crust.

Rubidium has few commercial uses and among these are the use of rubidium in radio tubes and photocells, and the use of radioactive rubidium to trace the flow of blood. Rubidium has been studied somewhat intensely in recent years and a few important potential applications have been found. One of the major problems of rubidium is the lack of uses.

BACKGROUND

Rubidium was identified in 1861 and had almost no industrial applications until the 1920's when small amounts were developed for use in photoelectric cells. During World War II, Germany extracted rubidium and cesium from residues from lithium operations; the rubidium was used for medical purposes and cesium for photoelectric cells.

Prior to 1958, outputs of rubidium and its compounds in the United States were a few hundred pounds annually but during that year some new technical-grade rubidium compounds were prepared from alkali carbonate residues of lithium operations, and the production of rubidium and its compounds noticeably increased.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

The rubidium-producing industry is small. Many firms have processed raw materials to rubidium primary products in the last few years, but most of this activity has stopped until the demand increases. During the period 1961–63, the producers of rubidium primary products were: Penn Rare Metals (subsidiary of Kawecki Chemical Co.), Revere, Pa., 1961–63; American Potash and Chemical Corp., Trona, Calif., 1961–63; MSA Research Corp., Callery, Pa., 1962; and Rocky Mountain Research Inc., Denver, Colo., 1962.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Rubidium (Rb) is soft, white, and the fourth lightest metal. It reacts violently with water and ice and ignites spontaneously when contacted with oxygen. Rubidium tarnishes rapidly in air and becomes coated with oxides. The molten metal ignites spontaneously in air. Some of its other properties are: Atomic number, 37; atomic weight, 85.48; density in solid form, 1.53 g./cm.^{3}; melting point, 38.5° C; boiling point, 688° C; and ionization potential of gaseous atoms, 4.16 volts.

ALKARB is a trade name given to a dry product formerly produced in San Antonio, Tex., from end liquor resulting from the extraction of lithium values from imported lepidolite. It consists of mixed alkali carbonates usually containing about 2 percent cesium and 20 to 25 percent rubidium carbonates. Lepidolite is no longer used to produce lithium compounds in the United States; consequently, ALKARB production ceased, but supplies are still available from accumulations.

[1] Commodity specialist.

Typical analyses of rubidium metal and rubidium compounds offered commercially are as follows (*7*):[2]

Element	Rubidium metal (liquid), percent		Rubidium compounds, percent
Rubidium	[1] 99.5	[1] 99.9	[1] 99.9
Sodium	[2] .05	[2] .01	[2] .01
Potassium	[2] .10	[2] .01	.005
Cesium	[2] .10	[2] .01	.01
Calcium	[2] .10	[2] .01	
Silica	[2] .01	[2] .005	
Iron and aluminum	[2] .01	[2] .001	.001
Calcium and barium			[2] .001
Lithium	[3]	[3]	[3]

[1] Minimum.
[2] Maximum.
[3] Not determined.

TECHNOLOGY

Mineralogy, Geology, and Mining

Rubidium and cesium often occur together in nature. The earth's crust has been estimated to contain 310 parts per million of rubidium while sea water contains about 0.2 part per million (*5*). The element occurs as an impurity in various minerals including lepidolite, pollucite, microcline, and biotite from granites and pegmatites, and carnallite from saline deposits. A field test for cesium and rubidium was developed to help prospectors identify the elements (*2*). Usually rubidium is found associated with one or more of the other alkali metals and occurs in greatest abundance in granites, granite pegmatites, and greisen. Samples of brine have been analyzed that contain up to 600 parts per million of rubidium.

Currently the commercial source of rubidium is mostly from accumulated stocks of ALKARB but a little from pollucite. Lepidolite, valued for its lithium and cesium content, is mined usually with other valuable pegmatite minerals by conventional opencut methods, or in some instances from underground operations. Most pollucite is probably recovered by hand-sorting methods.

Metallurgy

The historical process used on both lepidolite and carnallite residues comprises extraction of mixed crystals of rubidium and cesium alum from alkali residues by means of a series of ammonium alum precipitations. About 30 fractional recrystallizations are required subsequently to separate the more soluble rubidium alum from the cesium alum. In recent years two less expensive extraction methods have been used (*6*).

The chlorostannate method requires a partial separation of the potassium contained in the starting solution by dispersing carbon dioxide flue gas through the mixed alkali solution to precipitate potassium acid carbonate ($KHCO_3$). The remaining dissolved carbonates are converted to chlorides by adding hydrochloric acid and treated with enough stannic chloride to precipitate cesium chlorostannate, which is less soluble than its rubidium counterpart. Then the cesium-free chloride solution is treated with an excess of stannic chloride to precipitate rubidium chlorostannate. To purify the rubidium chlorostannate precipitate, it is dissolved in HCl and reduced to the stannous state. Chlorine gas is injected into the solution, resulting in reprecipitation of pure rubidium chlorostannate. The chlorostannate may be decomposed to separate the rubidium and tin chlorides by pyrolysis, by electrolysis, or by reducing the chlorostannate with iron and then adding sodium perchlorate to precipitate rubidium perchlorate which is decomposed to the chloride by heating.

The ferrocyanide method is used if the ferrocyanide or carbonate form is the desired rubidium end product. The mixed alkali carbonate liquor from the lepidolite plant is treated with sufficient sodium zinc ferrocyanide to precipitate cesium zinc ferrocyanide selectively. Then sodium zinc ferrocyanide is added in excess to precipitate rubidium zinc ferrocyanide.

The rubidium zinc ferrocyanide is decomposed and carbonated by heating in air, rubidium carbonate is water-leached from the roasted material, and the solution evaporated to dryness.

The simplest method of preparing the metal is by high-temperature vacuum reduction of the carbonate, hydroxide, or chloride. Rubidium carbonate or other compounds can be reduced by heating in vacuum or hydrogen with any one of several metals. An alternate method, seldom used commercially, is electrolytic reduction in fused-salt systems, using a rubidium compound such as the hydroxide, cyanide, or one of the halides as starting material.

USES

Only a few commercial uses have developed for rubidium, among them are the use of its compounds in radio vacuum tubes and photocells and of radioactive rubidium in medical testing as a "tag" element to trace the flow of blood. The latter use is increasing (*7*).

Rubidium and its compounds are so similar chemically to those of cesium that choice between them depends largely on which gives superior performance. Quantities of rubidium metal and compounds have been utilized in

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

research and in the development of applications. Potential uses for rubidium under consideration include use as a heat-transfer fluid and additive to gas in thermionic converters to convert heat directly to electricity, use of rubidium compounds as catalyzers in organic reactions, and small additions of rubidium to make glass more stable and durable (7).

ALKARB, a commercial source of cesium and rubidium, also has uses in glass, ceramic glazes, and porcelain enamels.

BYPRODUCTS AND ALTERNATE MATERIALS

Rubidium currently is being obtained from stocks of ALKARB, a byproduct derived from processing lepidolite to lithium compounds and no longer produced in the United States. Some rubidium also has been produced as a byproduct of processing pollucite to cesium. Lepidolite and pollucite are recovered from pegmatites which often yield other valuable minerals.

Pollucite might be able to substitute for ALKARB as a commercial source of rubidium when stocks of ALKARB become exhausted, but it would be costly to process pollucite only for rubidium.

The properties of rubidium are similar to those of the other alkali metals, but it is rarely used as a substitute for them because of its relatively high price.

Cesium, germanium, tellurium, selenium, silicon, and several other elements and compounds are alternate photosensitive materials.

RESERVES

Rubidium is much more abundant than either lead, copper, or zinc in the earth's crust, but very little information is available on natural concentrations of rubidium in potentially commercial deposits.

One of the largest known resources of rubidium in North America is reported to be that in pollucite in lithium-bearing pegmatite deposits at Bernic Lake, Manitoba, Canada. Tentatively, these deposits have been estimated to have 350,000 tons of pollucite containing 20 percent cesium and substantial rubidium oxide.

The principal domestic source of rubidium is ALKARB, a mixture of alkali carbonates derived from waste liquors resulting from processing certain imported lepidolite for lithium. Lepidolite has been reported to contain up to 3.5 percent Rb_2O, the rubidium being considered an impurity.

Large quantities of rubidium are reported in lepidolite and pollucite deposits in Southern Rhodesia, South-West Africa, and Mozambique.

Rubidium also exists in certain feldspars, brines, and saline deposits.

PRODUCTION, CONSUMPTION, AND TRADE

Statistical data on domestic rubidium are obtained by the Bureau of Mines through canvassing. Most of the data obtained are withheld to avoid disclosing company confidential information. Output of rubidium metal and compounds have fluctuated, sometimes sharply, but the long term trend is upward.

Import data on rubidium metal have been available since September 1963. No rubidium was imported during the last 4 months of 1963 or during 1964. No data are available on imports of rubidium compounds and exports of rubidium metal and compounds.

Pollucite is imported duty free. Rubidium metal and rubidium compounds are each dutiable at 10.5 percent, ad valorem.

STRATEGIC CONSIDERATIONS AND GOVERNMENT PROGRAMS

Producers of rubidium metal and compounds have easily met the small demand for these materials.

The United States is self-sufficient in ALKARB as long as the privately owned stock lasts, but when this supply is exhausted, rubidium output will have to rely much more on imports of pollucite and/or other domestic or foreign raw materials for sources of rubidium.

Rubidium is not on the list of materials for stockpiling in the national (strategic) and supplemental stockpiles.

PRICES

Prices quoted for 99+ percent rubidium during 1963 and 1964 were $390 to $425 per pound.

TRANSPORTATION AND SAFETY MEASURES (7)

Major precautions should be taken in handling, transporting and storing rubidium because it is very reactive with water and air. Rubidium is available in Pyrex glass ampoules or returnable stainless steel cylinders and is normally packed under argon or in vacuum.

Rubidium compounds are not particularly reactive; consequently, no special precautions in packaging these materials are necessary.

RESEARCH

Rubidium has been studied somewhat intensely in recent years in connection with heat transfer fluid, additive to the gas in thermionic converters which convert heat to electricity, and other applications.

The Bureau of Mines research on cesium and rubidium in recent years has been concerned with the development of concentration methods for pollucite (*3*, *4*), extraction and separation of cesium and rubidium from pollucite (*1*), purification of cesium and rubidium salts, and recovery of rubidium and other valuable metals from saline water.

OUTLOOK

Only moderate growth of rubidium production is predicted, although unforeseen large uses could develop as a result of technological advances.

The major rubidium source material in the United States will continue to be from the limited stock of rubidium-rich alkali carbonates derived from that portion of the lithium industry which formerly processed lepidolite to lithium. Some rubidium will be obtained from pollucite, and if necessary, from other materials.

Research will continue to be moderately sustained in developing the technology of rubidium and on the development of uses.

Occasional reductions in the price of rubidium metal and some of its compounds may occur if firm and larger demand for these materials would allow large scale production on a regular basis.

PROBLEMS

Rubidium's numerous problems extend from discovery of deposits through extraction and uses.

Rubidium occurrences are numerous particularly in pegmatite, brines, and saline deposits, but information is lacking on the nature and extent of rubidium in deposits. Consequently, the rubidium discoveries currently of commercial worth may not be competitive with subsequent discoveries.

Practically all domestically produced rubidium is being produced from stocks of byproduct alkali carbonates derived from processing imported lepidolite to lithium. The lithium industry no longer processes lepidolite, consequently there is no rubidium byproduct raw material being produced from this source.

Costly multistage extraction techniques employed to extract rubidium are largely responsible for the high prices of rubidium and its compounds.

The lack of complete data on the physical and chemical properties of rubidium hinders the development of uses. In addition, the alloying characteristics of rubidium, especially the development of intermetallic compounds, have not been extensively investigated.

Special precautions must be taken in preparing, handling, storing, and transporting rubidium as rubidium is extremely reactive. It ignites spontaneously in air and reacts explosively in water, and mists containing certain rubidium compounds are caustic. These costs contribute to high prices of rubidium.

Rubidium's high prices, uncertain supply, and not fully developed technology discourage the development of uses.

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SAND AND GRAVEL

By Perry G. Cotter [1]

THERE are more than 5,000 active producers of sand and gravel in the United States, and the output of sand and gravel, during the past two decades, has increased 250 percent. Total volume of production exceeds that of any other mineral commodity. Production is reported from every State, and latent or active deposits are located in almost all counties. Individual plants comprise small portable units, many of which produce less than 25,000 tons per year, and the multiunit operations of large corporations often associated with crushed stone plants, ready-mixed concrete plants, and slag processing, that individually produce in excess of 1 million tons annually. At the point of production, over 97 percent is valued at less than $1 per ton. Cost of transportation to markets may amount to much more than pit value and so markets are extremely confined. The volume and value of sand and gravel entering foreign trade is negligible.

The stability of the industry is evinced by its competence to produce increasing tonnages of this low-priced, bulky commodity to meet the various specifications of thousands of purchasers in all sections of the country. Few other producers of mineral commodities are faced with the number and complexity of the technical and economic problems inherent to the sand and gravel industry. However, the ingenuity of manufacturers of excavating, processing, and transportation equipment has assisted in keeping overall cost of production low, and research by various segments of the industry has developed profitable uses for materials formerly wasted. The upward trend of production is expected to continue, and yearly consumption by 1970 is estimated to be over 1 billion tons.

There are six factors to be considered in determining if a sand and gravel deposit can be profitably worked. (1) For what can the material be used? (2) Where are the potential markets, and what quantity can be sold? (3) What specifications as to particle size, shape, hardness, chemical composition, durability, texture, and freedom from impurities must be met? (4) For what price can it be sold? (5) What type of equipment is most efficient for mining and processing this sort of material? (6) What will it cost to prepare for market?

Some of the problems of the industry, low unit value, bulky nature of the product, and high transportation costs are universal. Others such as seasonality of operation, influence of day-to-day weather changes, stockpiling and reclamation, disposal of waste water and undersized material, changes in specifications and in market areas, together with restrictive zoning legislation may be more localized.

BACKGROUND

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Nearly 6,000 sand and gravel operators reported production in 1963. As shown in figure 1, over 822 million tons was produced that year, outranking any other mineral product in output.

Firms in the industry range from one-man roadside operations to large corporations with 20 or more producing plants. The industry has become highly mechanized and produces about 65 tons a man-day. About 89 percent of the production enters the construction industry as fine or coarse aggregate.

Deposits of sand and gravel occur in every State in varying abundance. Local shortages of suitable material occur in many areas, such as in sections of Tennessee, Texas, and Loui-

[1] Commodity specialist.

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siana where sand is practically nonexistent, too expensive, or unsuitable for construction. In Florida sand is abundant, but generally too fine for concrete sand, and gravel is virtually absent.

Due to the wide distribution, low cost, and bulkiness of sand and gravel, development has occurred near points of consumption where materials meeting the requirements are available. Some special grades, however, cannot be prepared from any ordinary sand deposit, and shipments are often made over considerable distances.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Sand and gravel are disintegration products of rocks. Although the term *sand* is commonly understood to refer to quartz sand, or silica, that predominates in natural deposits, it basically refers to size, and the term sand also is applied to other materials as black sands, zircon sands, slag sand, stone sand, and many others. Gravel that has not been subjected to all the abrasion and decomposition processes which produce sand may contain more of the original rock constituents such as mica, feldspar, olivine, shale, iron compounds, and calcareous minerals. Many of the size classification scales for sand and gravel are based upon that of Wentworth shown in table 1 (*15*).[2]

TABLE 1.—*Wentworth grading of sand and gravel*

Term	*Size (millimeters)*
Boulders	256+
Cobbles	64–256
Gravel	4–64
Granules	2–4
Sand	0.0625–2
Silt	0.0039–0.0625

The earliest recorded specification for sand is that of Vitruvius, (*14*) in the first century B.C., who stated that for testing masonry sand, "throw some sand upon a white garment and then shake it out; if the garment is not soiled and no dirt adheres to it, the sand it suitable." Since that time, because of the multitudinous uses of silica sand and gravel, the number and variety of tests and specifications have expanded greatly. Specifications now require tests for soundness, freedom from deleterious particles, resistance to freezing and thawing, adhesion of bitumens, size gradation, and many others. Specifications are written by users of foundry sand, (*3*) manufacturers of abrasives, glass, chemicals, ceramics, by building associations, governmental agencies, highway engineers, and the American Association for Testing and Materials.

For most glass products manufacturers prefer a sand with a minimum of iron oxide and chromium compounds. High percentages of alumina and calcium or magnesium oxides are also undesirable. It is generally agreed that all grains should pass a No. 20 sieve.

Sand for use in construction of bituminous and concrete roads must be clean, hard, and free from clay. For concrete pavements mixtures of coarse and fine sands are preferred, and the sand must be totally free from organic impurities. For bituminous paving and for wearing courses, the presence of small amounts of organic material is allowable. Specifications for paving sands are published in detail by Federal and State highway officials, industrial organizations, and contractor's associations (*2, 7–8, 12*).

Specifications for construction gravel are published by these groups along with standard test methods for grading (*5*).

Standards set for sand and gravel used in roadbuilding and concrete construction tend to become more specific and rigid as regards shape, physical properties, and screen sizing.

Sand used in filtration beds of municipal water plants must be of uniform grade, free from clay, loam, dust, or other foreign matter, and must possess good permeability.

For blast sands, used in cleaning castings, stone buildings, and for carving designs and lettering on stone, the ability to resist shattering and uniform grade are most important.

Glass sands for the manufacture of flat glass, table glass, and optical glass must contain 99 percent or more silica, and a minimum of coloring substances such as chromium or iron, and be of uniform grade. Specifications for common colored-glass bottles are less rigid, and these sands may contain as much as 1 percent of coloring materials. For high-grade chemical and optical equipment, either pure quartz or vitreous silica are used. Standard methods for the chemical analysis of glass sands are described under ASTM designations C–146–43 (*6*).

TECHNOLOGY

Geology

Most of the commercial sand and gravel deposits in the Northern and Eastern United States are the results of glacial disintegration and abrasion of bed rock. Upon recession of the glaciers, the transported material was deposited in the form of moraines, drumlins, eskers, and kames and further abraded, transported, and segregated by the action of running

[2] Italicized numbers in parantheses refer to items in the list of references at the end of this chapter.

water. Specific understanding of the processes which entered into the formation of particular deposits of sand and gravel is fundamental in attempts to locate such deposits, particularly as they are frequently hidden by overburden. If a deposit consists largely of hard, well-rounded pebbles, the inference is that the material has been transported for a long distance; the obverse may be assumed if the gravel is angular and poorly classified. Material deposited directly from glaciers with little working over by water, as in mountainous areas, may exhibit large irregularities in quality and size. Material from such deposits requires considerable processing to remove unwanted fines and must be crushed to meet size specifications. Fluvioglacial deposits, on the other hand, generally contain less clay, are better classified or sorted, and resemble stream deposits, although alluvial fans may contain highly segregated material along with clay and silt because the glacial streams, which deposited the fans frequently shifted channels and were subject to wide variations in the volume of water received. In the Central and Far Western States stream deposits, often replenished by periodical floods, are an important source of sand and gravel. Marine and lake deposits consist of well-rounded pebbles and fine sand, but are commonly contaminated by particles of calcareous shells and organic matter. Dune sands, formed by wind action, and occurring at various places along the Atlantic and Pacific coasts, the southern end of Lake Michigan, and in central Colorado have, so far, been of little economic value. In a few areas there are deposits of sand and gravel of exceptional depth and extent. Mined for many years, these sands and gravels have been named from the localities in which they were first developed, as Ottawa sand, Portage sand, Albany sand, or from the geological horizons in which they occurred as St. Peter sand, Tertiary gravel, and Quaternary sands and gravel.

To summarize, most commercial sands and gravels are obtained from thickly bedded deposits covered by little or no overburden and they must be worked economically where they are found.

Mining

Excavation of sand and gravel deposits is accomplished by means of a wide assortment of equipment; power shovels, bulldozers, front-end loaders, digging wheels, draglines, dredges, hydraulic monitors, and many others. Most large producers use combinations of digging equipment.

Hydraulic dredges, designed for excavating from river, lake, and ocean deposits, may wash, screen, and otherwise process the material upon the dredge, and then transport it to stockpiles. Others may pump the unprocessed material to shore installations. Fine sands, used for fill, are frequently excavated by dredges and pumped for several miles. Unconsolidated glass sand deposits may be excavated by hydraulicking. This involves pumping water, under high pressure, against a bank and then removing the slurry by a solids pump to a stationary plant for screening and sizing. Portable plants, designed to combine crushing, screening and conveying equipment, and operated by a few men, produce sand and gravel from deposits of limited extent, and usually for local use.

Processing

Although small amounts of unprocessed bank run sand and gravel are used for fill the larger part of U.S. production is partially or totally processed. Early methods simply screened the material to separate sand and loam from the coarser gravels. Present methods demand washing with water during the screening process, followed by crushing of the larger aggregate in cone or gyratory crushers, or in some cases, jaw or impact crushers when cubical aggregate is specified. Secondary crushing is usually done by cone crushers, although many self-contained portable plants use roll crushers. Screening is done, in most plants, by horizontal or sloped vibratory screens or multidecked screens frequently heated to prevent clogging. For some river deposits, contaminated by coal refuse or other deleterious materials, heavy-media separation or jigging equipment is used. Sand, for use in construction, is freed from clay by log washers or by rotary scrubbers. The scrubbing is followed by classifiers, separatory cones, hydroseparators to remove water, and fine screens for grading. Removal of processed sand and gravel from the processing plant to stockpiles or bins is accomplished by flexible combinations of conveyor belts, bucket elevators, and screw conveyors (*4*, *10*).

Most natural sands are deficient in the small grain sizes now demanded by the building trades, and such sands may be further reduced in size by ball mills.

USES

Extensive utilization of sand and gravel in concrete for construction of buildings and for concrete and bituminous paving accounts for 96 percent of total production. Of the total Government-and-contractor production, 97 percent is used for roads.

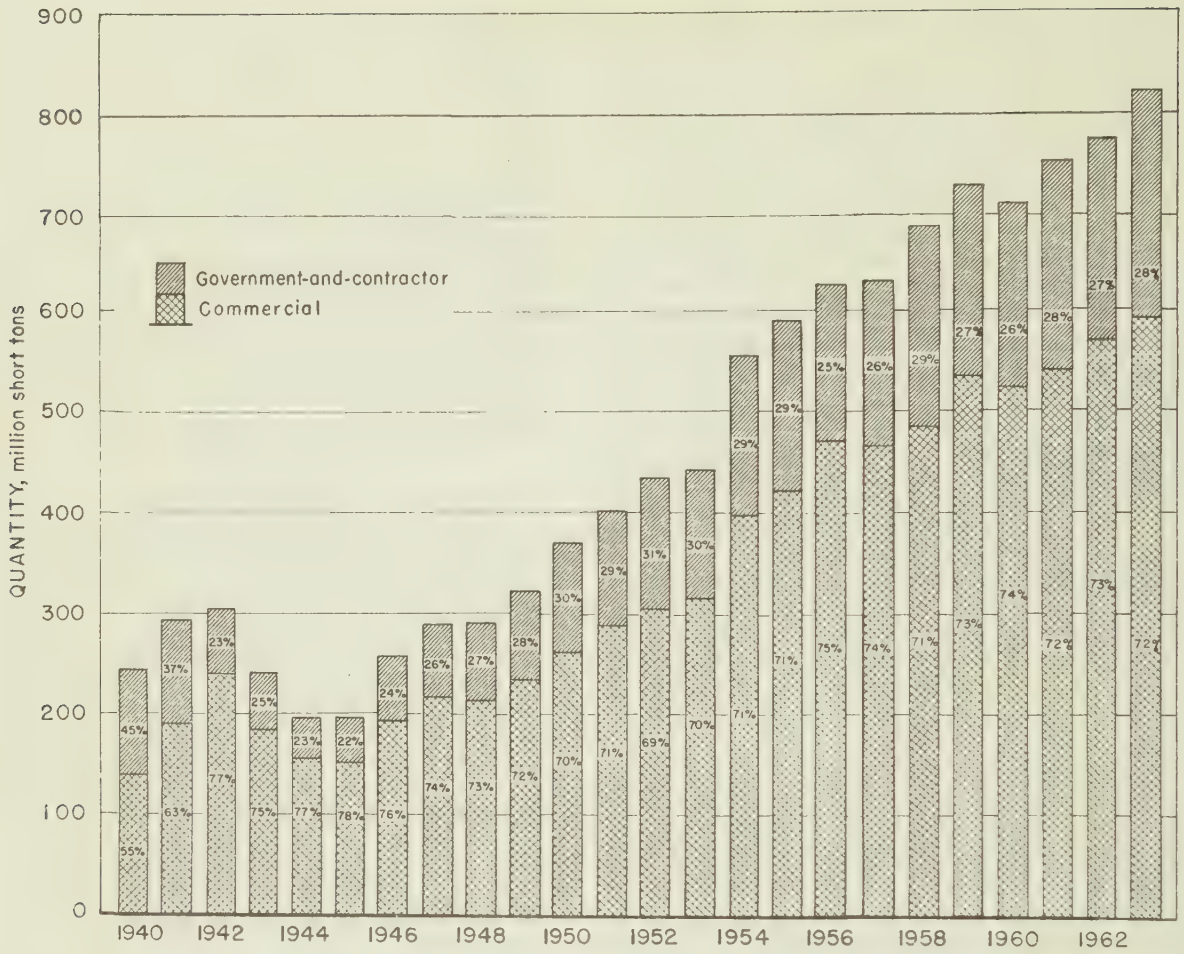

FIGURE 1.—Sand and Gravel Sold or Used in the United States, by Producers.

The glass industry is one of the most important users of the higher priced industrial sands. Sands used for glassmaking must meet definite specifications for both grain size and chemical composition.

Large tonnages are used in iron and steel foundries to make molds for castings. Natural molding sands, usually containing 8 to 20 percent clay, are a distinct product of the industry as are many other types used for steel castings, for the casting of nonferrous alloys, and for mold facings.

Smaller amounts are used for ceramics, in stone sawing, sandblasting, glass grinding, stone polishing, as fillers in paints, plasters, cements, and as abrasive material in soaps and polishing compounds. The chemical industry uses silica in the manufacture of sodium silicate, silica gels, calcium silicate, silicon tetrachloride, and in a wide variety of silicones.

Filter sands, used in municipal water plants, must be of uniform grain size within limits designed to allow maximum pore space for rapid filtration. They must also be free from mineral constituents which could react with chemicals used in water treatment.

Table 4 shows U.S. production of sand and gravel by end use.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

In metropolitan areas the sale of top soil, produced in the course of removing overburden from sand and gravel deposits, is an important factor in making sand and gravel operations profitable. Many producers have installed plants for manufacturing concrete blocks, facing panels, ready-mixed concrete, facing aggregate, and other construction materials.

ALTERNATE MATERIALS

Crushed stone, iron-blast-furnace slag, and fly ash are used to implement or replace sand and

gravel in some types of construction. As these alternates are sold at prices comparable to those received for sand and gravel and transportation costs may be lower, competition for markets is keen, although many producers of building materials stock all types of aggregates.

Stone sand produced by marble and granite processors is frequently used to replace natural sand in masonry work, and larger sized chips from the same processors find a ready market for exposed aggregate panels.

Chemical stabilization of clay subsoils with lime and cement is of growing importance and decreases demand for sand in some areas.

Lightweight aggregates, produced by bloating clays or shales, are in greater demand for use in the manufacture of concrete blocks to be used where load-bearing properties are of minor importance.

RESERVES

Because of the relatively low unit value of sand and gravel, deposits are seldom surveyed in depth to determine reserves. However, as a generality, it may be stated that resources of sand and gravel are sufficient to meet the demand created by any foreseeable expansion in the national economy. This does not mean that good construction sand and gravel is available in quantity in every area nor that all marginal deposits can be processed to supply satisfactory aggregate. The yearly production of nearly 1 billion tons of sand and gravel, most of which is used in metropolitan areas, has reduced supplies near some large cities to the point where these commodities must be secured from greater distances with accompanying higher costs. Rapid and undirected surburban growth has eliminated many potential reserves, not only by restrictive zoning ordinances, but by overspreading deposits with roads, houses, apartments, and business districts. Reserves of higher priced industrial sands, purchased for future development, are menaced by the rapid expansion of rural zoning restrictions.

CONSERVATION

Because of the assumed abundance of sand and gravel, few definite measures have been taken toward conservation, as the supply generally has been considered adequate except in deposits near large cities. To utilize available supplies in such areas, increasing depths of overburden are being removed and lower grade deposits are being worked.

Indirectly, a measure of conservation can be considered as a result of using portable plants that are able to mine small, scattered deposits, near points of application. These deposits that formerly were of no economic value supplement larger deposits and increase reserves.

Little or no regard has been given to the various ideas advanced for multiple land use in which sand and gravel deposits are removed prior to construction of schools, housing developments, and shopping centers.

SOURCES OF STATISTICAL INFORMATION

Statistical data published by the Bureau of Mines on production, value, uses, employment, and technical aspects of operations are acquired from the individual producer on a voluntary basis and from the Governmental agencies for which material was produced.

PRODUCTION, CONSUMPTION, AND TRADE

The continued increase in population with resulting demands for homes, industrial buildings, highways, defense, public works, and industrial uses has given impetus to the sand and gravel industry. The national road building program offers opportunities for even greater utilization of sand and gravel.

The construction industry utilizes most sand and gravel produced and is mainly responsible for the doubled annual tonnage and dollar volume over the past decade.

Sand and gravel production is divisible into two main classes; commercial production which consists of a particular plant's output with at least part of the material sold on the open market, and Government-and-contractor production which is produced exclusively for use on Federal, State, county, or municipal projects. If part of the production from a particular plant is sold commercially, the entire output is placed in the commercial category.

Table 5 presents general data on production by size of plant. Statistical data are given each year in the Minerals Yearbook chapter on sand and gravel. The terms "consumption" and "production" are used interchangeably, as stocks are relatively small and constant.

Sand and gravel are not major commodities in foreign trade. Glass sand is sometimes imported, as well as certain types of molding sand, which is still preferred by some users. Some ballast sand enters the country, and there is some movement across borders of ordinary sand and gravel for local use.

Over 1 million tons of sand and gravel was exported to Canada, in 1963, having an average value of $2.67 per ton.

Crude sand and gravel enter the United States duty free. Glass sand with less than 0.06 percent Fe_2O_3 is dutiable at 50 cents per ton. The quantity imported is small and usually consists of specialized sands such as the Belgium glass sand imported for making optical glass.

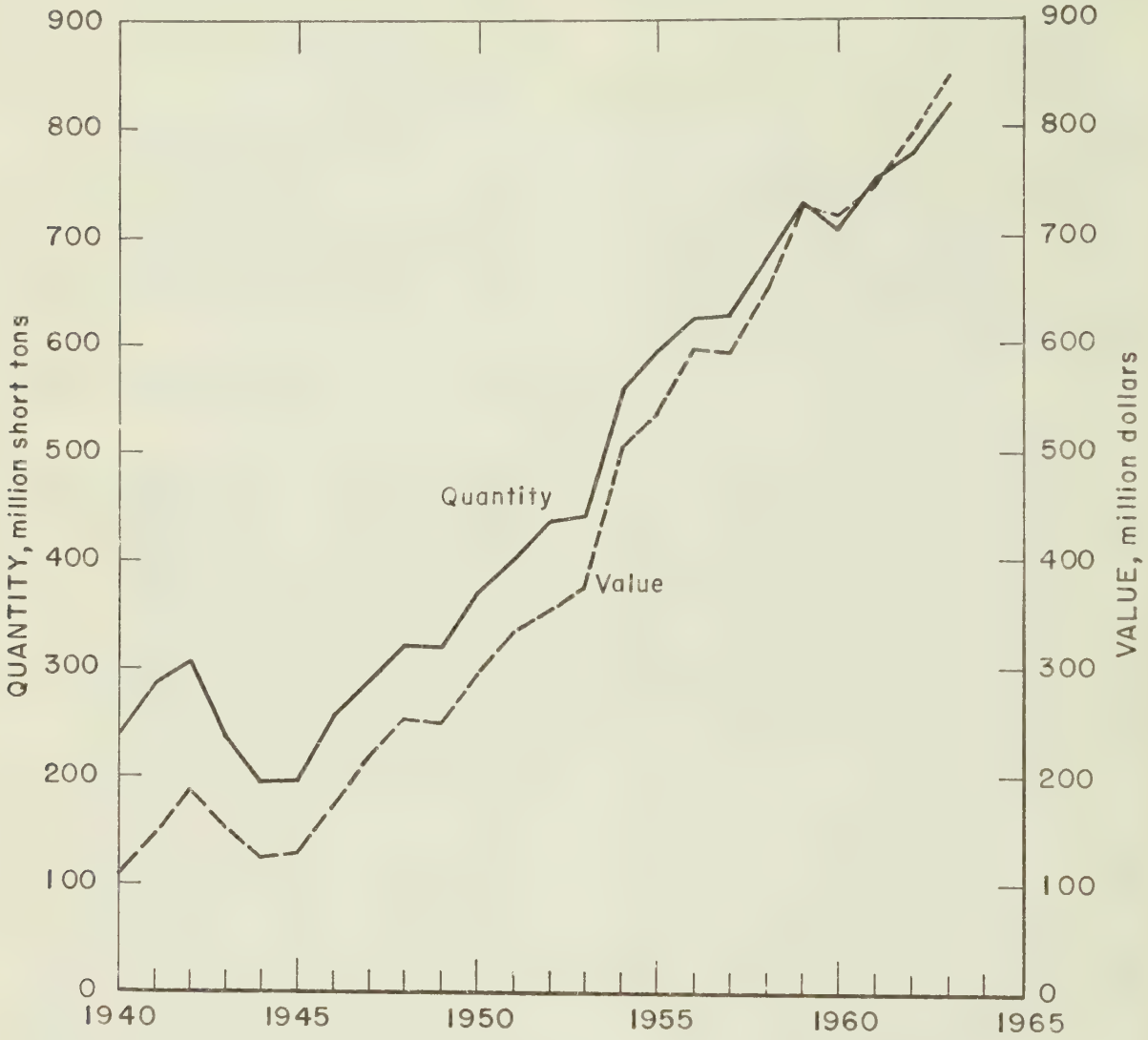

FIGURE 2.—Production and Value of Sand and Gravel in the United States.

TABLE 2.—*Sand and gravel sold or used by producers in the United States, by States*

[Thousand short tons and thousand dollars]

State	1962		1963	
	Quantity	Value	Quantity	Value
Alabama	4,655	$4,486	5,362	$5,778
Alaska	5,731	5,355	16,924	22,006
Arizona	15,579	17,404	15,037	14,468
Arkansas	10,847	10,006	12,099	13,589
California	107,660	124,922	112,188	128,175
Colorado	19,313	18,926	20,385	20,926
Connecticut	10,208	9,244	10,504	9,342
Delaware	1,755	1,445	1,095	1,136
Florida	5,924	5,179	7,542	5,822
Georgia	3,429	3,365	3,817	3,922
Hawaii	700	1,122	304	763
Idaho	14,321	13,029	12,432	10,614
Illinois	34,122	38,981	31,750	36,432
Indiana	21,261	18,692	22,841	20,682
Iowa	13,797	12,474	14,168	12,845
Kansas	11,552	8,039	12,062	8,676
Kentucky	6,137	5,378	6,479	6,071
Louisiana	12,040	14,817	12,500	14,701
Maine	10,014	4,013	11,196	4,673
Maryland	12,762	16,816	13,309	16,061
Massachusetts	17,566	15,026	19,905	15,595
Michigan	47,563	42,029	50,459	43,430
Minnesota	29,399	22,656	30,460	23,318
Mississippi	7,001	7,262	6,825	7,056
Missouri	10,304	11,572	10,653	12,260
Montana	18,473	17,642	14,320	13,755
Nebraska	12,853	9,797	11,167	10,682
Nevada	7,850	9,655	9,688	10,512
New Hampshire	8,260	4,119	7,583	4,377
New Jersey	13,728	21,230	16,672	25,245
New Mexico	6,889	8,021	8,403	12,844
New York	29,447	31,346	37,379	37,279
North Carolina	12,516	11,457	11,025	10,133
North Dakota	9,615	7,122	9,531	9,193
Ohio	35,204	43,333	37,790	44,368
Oklahoma	4,436	4,736	5,420	6,116
Oregon	14,869	14,556	15,715	18,850
Pennsylvania	14,419	23,587	14,066	23,538
Rhode Island	2,346	1,890	1,750	1,840
South Carolina	3,318	3,670	4,051	4,751
South Dakota	15,371	9,207	20,807	16,315
Tennessee	6,075	8,018	7,613	9,443
Texas	30,076	33,097	33,256	36,311
Utah	19,941	20,954	11,710	10,411
Vermont	1,430	1,076	2,374	1,409
Virginia	9,745	16,375	10,399	17,754
Washington	19,580	18,145	22,763	20,488
West Virginia	5,202	10,942	4,808	10,579
Wisconsin	33,649	24,408	35,633	26,348
Wyoming	7,769	8,104	7,901	7,875
Total	776,701	794,725	822,000	849,000
American Samoa	3	4	77	193
Panama Canal Zone	70	77	84	87
Puerto Rico	7,378	9,793	7,616	10,407

TABLE 3.—*Sand and gravel sold or used by producers in the United States*

[Thousand short tons and thousand dollars]

Year	Sand		Gravel		Total				Grand total	
	Noncommercial	Commercial	Noncommercial	Commercial	Sand		Gravel		Sand and gravel	
	Quantity	Quantity	Quantity	Quantity	Quantity	Value	Quantity	Value	Quantity	Value
1954–58 (average) [1]	24,139	201,651	145,296	247,302	225,790	$232,756	392,598	$345,063	618,388	$577,819
1959	37,618	231,554	157,354	303,369	269,185	288,531	461,020	440,181	730,205	728,712
1960	31,517	234,139	155,380	288,756	265,656	293,599	444,136	426,833	709,792	720,432
1961	42,990	240,346	169,239	299,209	283,336	303,549	468,448	447,752	751,784	751,301
1962	40,671	259,086	169,051	307,893	299,757	328,563	476,944	466,162	776,701	794,725
1963	40,836	271,728	190,343	319,213	312,564	339,396	509,556	509,361	822,000	849,000

[1] Includes possessions and other areas administered by the United States (1954–56).

TABLE 4.—*Sand and gravel sold or used by producers in the United States [1] by uses*

[Thousand short tons and thousand dollars]

Use	1954–58 (average)		1959		1960		1961		1962		1963	
	Quantity	Value	Quantity	Value	Quantity	Value	Quantity	Value	Quantity	Value	Quantity	Value
Sand:												
Glass sand	6,196	$17,905	6,251	$20,122	6,449	$21,642	6,682	$21,943	7,199	$23,847	7,204	$23,626
Molding sand	7,125	14,905	6,246	15,144	6,063	16,001	5,815	15,808	6,981	18,771	7,579	20,814
Building sand	106,666	101,920	123,237	128,122	122,845	127,972	125,290	132,000	134,249	140,507	140,352	145,362
Paving sand	85,099	68,246	104,700	88,424	99,391	91,742	108,788	95,866	111,110	100,410	113,346	102,169
Grinding and polishing sand [2]	1,641	4,887	1,874	5,654	1,702	5,333	1,729	5,202	1,789	5,138	1,894	5,860
Fire or furnace sand	541	1,126	534	1,188	559	1,214	622	1,285	396	945	568	1,082
Engine sand	1,276	1,677	873	1,535	890	1,683	754	1,477	777	1,588	838	1,659
Filter sand	528	862	395	934	269	624	210	547	176	457	297	756
Railroad ballast sand	750	410	990	534	622	468	517	354	825	880	444	344
Other sand [3]	15,968	20,818	24,085	26,874	26,866	26,920	32,929	29,067	36,255	36,020	41,726	38,313
Total sand	225,790	232,756	269,185	288,531	265,656	293,599	283,336	303,549	299,757	328,563	314,248	339,985
Gravel:												
Building gravel	99,802	115,325	114,190	142,371	108,149	136,152	111,378	146,188	111,712	145,257	118,357	149,870
Paving gravel	263,399	207,886	313,475	271,485	289,559	258,860	311,714	271,704	318,972	289,701	326,437	308,031
Railroad ballast gravel	7,604	5,213	4,812	3,695	4,650	3,810	3,232	2,570	3,625	2,718	3,509	2,898
Other gravel [4]	21,793	16,639	28,543	22,630	41,778	28,011	42,124	27,290	42,635	28,486	59,569	47,973
Total gravel	392,598	345,063	461,020	440,181	444,136	426,833	468,448	447,752	476,944	466,162	507,872	508,772
Total sand and gravel	618,388	577,819	730,205	728,712	709,792	720,432	751,784	751,301	776,701	794,725	822,000	849,000

[1] Includes territories, possessions, and other areas administered by the United States, 1954–56. Includes Alaska and Hawaii in 1957–63.
[2] Includes blast sand.
[3] Includes sand for fills and similar purposes, 1956–58; also includes ground sand, 1954–58.
[4] Includes gravel for fills and similar purposes.

TABLE 5.—*Number and production of domestic commercial sand and gravel plants by size of operation*

Annual production (short tons)	1962				1963			
	Plants [1]		Production		Plants [1]		Production	
	Number	Percent of total	Thousand short tons	Percent of total	Number	Percent of total	Thousand short tons	Percent of total
Less than 25,000	1,876	35.9	18,604	3.3	2,528	43.3	51,217	8.7
25,000 to 50,000	912	17.5	32,960	5.8	895	15.3	32,702	5.5
50,000 to 100,000	939	18.0	66,826	11.8	896	15.4	64,410	10.9
100,000 to 200,000	744	14.3	103,624	18.3	756	13.0	103,874	17.6
200,000 to 300,000	322	6.2	78,267	13.8	301	5.1	73,542	12.4
300,000 to 400,000	158	3.0	53,248	9.4	150	2.6	51,154	8.6
400,000 to 500,000	80	1.5	35,365	6.2	85	1.5	36,998	6.3
500,000 to 600,000	48	.9	24,743	4.4	44	.7	24,054	4.1
600,000 to 700,000	37	.7	22,364	4.0	65	1.1	24,526	4.1
700,000 to 800,000	16	.3	12,001	2.1	23	.4	17,263	3.0
800,000 to 900,000	21	.4	17,730	3.1	22	.4	18,690	3.1
900,000 to 1,000,000	8	.2	7,537	1.3	16	.3	15,275	2.6
1,000,000 and over	60	1.1	93,710	16.5	54	.9	77,236	13.1
Total	5,221	100.0	566,979	100.0	5,835	100.0	590,941	100.0

[1] Includes a few companies operating more than 1 plant but not submitting separate returns for individual plants.

TABLE 6.—*U.S. imports for consumption of sand and gravel by classes*

Year	Sand				Gravel		Total	
	Glass sand [1]		Sand, n.s.p.f., crude or manufactured					
	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value
1954–58 (average)	3,636	[2] $390,754	305,896	[3] $412,042	5,348	[3] $6,253	314,880	[3] $719,049
1959	101	[3] 91,414	348,331	463,589	102,878	92,967	451,310	647,970
1960	10,765	37,111	379,673	515,837	3,752	5,423	394,190	558,371
1961	2	[2] 1,602	335,905	440,759	43,287	44,009	378,294	486,370
1962	31,416	63,950	307,637	414,703	29,198	31,948	368,251	510,601
1963	22,724	68,650	336,547	430,165	(4)	(4)	359,271	498,815

[1] Classification reads, "Sand containing 95 percent or more silica and not more than 0.6 percent oxide of iron and suitable for manufacturing glass."
[2] Consists mainly of synthetically prepared silica from West Germany for specialized uses and is not comparable in value to ordinary glass sand.
[3] Data known not to be comparable with other years.
[4] Sand, n.s.p.f., crude or manufactured and gravel no longer separately classified.

Source: Bureau of the Census.

STRATEGIC CONSIDERATIONS

Although sand and gravel are of vital importance to the construction and other industries, including building of landing strips for aircraft, for missile bases, shelters, and other defense facilities, the industry is not concentrated in any one locality. In case of attack, transportation of sand and gravel to point of use would be a major problem.

PRICES

Except for minor amounts of bank-run sand and gravel produced by Government-and-contractor operators for road fill, all construction sand and gravel is now processed to meet exacting specifications.

The average value for commercially produced sand and gravel in 1963 was $1.12 per ton, the same as in 1962; that for Government-and-contractor production was $0.81, an increase of $0.05 per ton. Representative prices per ton for construction sand in various metropolitan centers were as follows: Birmingham, $1.30; Boston, $3.00; Chicago, $4.13; Denver, $1.42; Minneapolis, $1.70; New York, $2.45; and San Francisco, $2.35.

TAXES

Depletion allowances applicable to the sand and gravel industry, based on gross income and apportioned according to the quantity sold in each category, are 5 percent for sand and gravel used for construction purposes and 15 percent for industrial sand and gravel.

TRANSPORTATION

Sand and gravel has a relatively low value per ton; therefore, transportation factors loom large in the economics of the industry and sometimes make up more than two-thirds of the selling price. There has been a marked trend toward increased truck transportation for many years. It is conceivable that the railroads might win back some of their lost haulage as plants are removed farther from metropolitan centers. On the other hand, the tendency toward utilization of portable plants has shortened the distance of transport. The imposed restrictions on the wheel-load that are permitted over highways forbid the use of trucks on the road that are required in some pits.

In order to lower transportation rates for the sand and gravel industry and allow haulage to market from greater distances, some railroads are installing unitized train systems.

RESEARCH

Research is conducted by the National Sand & Gravel Association on methods for prospecting for sand and gravel deposits, processing, and rehabilitation of worked-out areas. Others actively engaged in research to develop new uses or to improve specifications are the Portland Cement Association, the National Lime Association, Asphalt Institute, Bureau of Public Roads, U.S. Army Corps of Engineers, Bureau of Reclamation, National Ready Mixed Concrete Association, Bureau of Mines, various State universities, highway departments, and many others. Manufacturers of excavating and processing machinery conduct research to develop more efficient machinery and reduce wear on crushers and screens.

OUTLOOK

In spite of the marked trend toward increased use of lightweight aggregate and aerated concrete, to construct lighter buildings, and in the use of glass, metals, and plastics for ornamentation, major construction programs will continue to be essentially dependent upon supplies of large amounts of low-priced raw materials such as sand and gravel. Moreover, demand for the higher priced specialty sands used in glassmaking, in refractories, in metallurgy, and by the chemical industry may be expected to increase. Continuation of the Federal highway program, originally scheduled to be completed in 1972, may be expected, with expansion of programs for interstate and primary systems and modernization of many ABC roads. Increased production of aggregate will be required to supply this demand as well as for construction of new schools, industrial plants, sewage and water treatment plants, homes and apartments. Based upon forecasts of increases in national income, population, and demand for various types of housing, production of sand and gravel in 1980 may be expected to be about 1.8 billion tons. However, it should be noted that the unit price may continue to be low, that specifications will tend to become more stringent, that operations in many areas will be dependent upon the seasonal activity of the construction industry, and that

suburban growth, although supplying new marketing areas, may also curtail some operations through restrictive zoning legislation.

The trend toward firmer specifications will require better product control, including stricter attention to sizing, blending, and removal of deleterious substances.

No new uses are foreseen for the great volume of sand and gravel used in construction, but new applications for chemical products derived from silica, and expansion of use in paints, silicone rubber, plastics, paper, pharmaceuticals, and as dehydrating agents, will increase markets for high-grade silica.

PROBLEMS

The production of large quantities of sand and gravel from sources very near markets, at a price low enough to compete with alternate building materials such as crushed stone, slag, and lightweight aggregate, is a major problem for operators. Most sand and gravel is used within 25 miles of the point of production and in metropolitan centers where zoning regulations and transportation problems are complicated. Operative deposits are rapidly depleted in these areas, and development of new deposits is restricted by construction of buildings which submerges them.

Few other sectors of the mineral industry are so subject to seasonal influences or to the daily changes in production schedules caused by the construction industry's dependence upon the weather.

Sand and gravel occur in the same deposits, but the relative proportions of each vary over a wide range, from cobblestones to silt. Consequently the problem of producing aggregate to rigid specifications is difficult and involves combinations of many types of equipment; crushers, screens, washers, classifiers, and grinding mills. Many operators are unaware of methods by which much of this processing equipment may be most efficiently used. In addition, the wide range of specifications for construction sand and gravel set by Federal, State, and other government agencies, multiplies the difficulties faced by operators who attempt to furnish aggregates of a specified size distribution.

With increased demand for washed aggregate, the problem of securing adequate supplies of wash water has been intensified with the accompanying problem of waste water disposal (*9*).

The elimination of dust and noise from sand and gravel operations has been the subject of much research, but results of this research are not widely disseminated, although application of such control methods might assist in reducing the growing demand for restrictive zoning legislation.

The problems of land-use planning to allow extraction of sand and gravel before such deposits are lost forever by covering them with buildings are receiving some consideration (*1*, *13*), and research is continuing on methods for rehabilitating worked out sand and gravel pits (*11*).

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SCANDIUM

By Donald E. Eilertsen [1]

SCANDIUM is one of the few elements that is still a laboratory curiosity. Recovery of a full pound of scandium, the largest amount ever to exist in one place at one time, made scientific news in January 1960.

At present very few uses have been developed for scandium. In recent years, three firms have produced scandium and its compounds; sales of scandium oxide in 1962 were less than 30 pounds. Scandium prices are high; the demand is small. The resource of scandium in uranium ores and phosphate deposits is very large. The most acute problem of scandium is the almost complete lack of uses.

BACKGROUND

The element scandium was predicted in 1871 and separated from gadolinite in 1879. Little attention was given to the element for many years. In the late 1950's the U.S. Air Force sponsored research to gain a better understanding of its physical and mechanical properties for possible usage. The scandium for study was produced at The Metals Research Laboratories of Union Carbide Metals Co. from scandium fluoride purchased from Heavy Minerals Co. (*2*).[2] Meanwhile the Bureau of Mines began studies on sources and recovery of scandium from uranium mill solutions. Some of this work was in cooperation with Vitro Chemical Co. and led to experimental production of scandium as a byproduct in processing uranium ores.

SIZE AND ORGANIZATION OF THE INDUSTRY

The scandium-producing industry is relatively small. The major producers in recent years are American Scandium Corp., Newtown, Ohio (metal and oxide); Research Chemicals Division, Nuclear Corporation of America, Phoenix, Ariz. (oxide); and Michigan Chemical Corp., St. Louis, Mich. (oxide).

PROPERTIES (*1*)

Scandium (Sc) has properties similar to yttrium and lanthanum. The chemical and physical properties of scandium are gradually becoming known as a result of recent research.

Scandium, silvery white but slightly yellow after exposure to air, has the following properties: Atomic number, 21; atomic weight, 44.96; melting point, 1,539° C; boiling point, 2,727° C; density, 2.99 grams per cubic centimeter; heat capacity (25° C), 6.01 calories per mole per °C; heat of fusion, 3.85 kilocalories per mole; heat of vaporization at 1,630° C, 78.6 ± 0.7 kilocalories per mole; linear coefficient of expansion (0 to 900° C), 12×10^{-6} per degree; crystal structure to 1,335° C, hexagonal close packed; atomic volume, 15.0 cubic centimeters per mole; and metallic radius, 1.64 A.

Scandium does not tarnish quickly in air, nor is it attacked quickly by water, but it reacts quickly with acids. Scandium has been successfully rolled, swaged, and welded.

TECHNOLOGY

Mineralogy and Geology

The earth's crust contains an estimated 5 parts per million (ppm) of scandium, the same as for arsenic. Sea water contains about 0.00004 ppm of scandium. Thortveitite, $(Sc,Y)_2 \cdot Si_2O_7$, the only known mineral that is usually rich in scandium, can contain almost 35 percent of the element. For many years a Norwegian firm produced thortveitite concentrate containing approximately 20 percent scandium.

In a survey of scandium occurrences (*5*), samples of pegmatites contained 5 to 20 ppm of scandium; coal ash and zinc plant residues,

[1] Commodity specialist.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

10 to 30 ppm and monazite, euxenite, zircon-bearing sandstones, thorite ores, ferberite tungsten ores, and laterite nickel ores, 30 to 100 ppm. Certain samples of wolframite tungsten mineral concentrate contained 500 to 800 ppm of scandium, while phosphoric acid solutions contained 6 to 20 ppm. Solutions from uranium mills that used acid-leach processes contained 0.2 to 1 ppm of scandium. Iron sludge from intermediate material of uranium mills using an organophosphate solvent extraction procedures contained 1,000 to 1,800 ppm of scandium.

Extraction (*3*)

In uranium recovery operations of Vitro Chemical Co., scandium was found to follow uranium in solvent extraction operations using a dodecyl phosphoric acid in kerosine as the organic solvent. Scandium did not strip with the uranium but remained in the solvent, thus increasing the concentration of scandium in the organic phase with recycling. After this was discovered, provisions were made to recover a scandium-bearing concentrate.

Ore was crushed, ground, and leached with dilute sulfuric acid. Addition of an oxidant assured conversion of uranium minerals to soluble form for undergoing solvent extraction. For scandium concentrate recovery, part of the stripped solvent was fed to the hydrofluoric strip section of the plant. The scandium content was less than 0.1 gram of scandium sesquioxide (Sc_2O_3) per liter in the organic. A two-stage countercurrent solvent extraction system with acid fluoride solution was used to treat the solvent, the main aqueous stream of which was filtered to remove a scandium-thorium fluoride cake containing about 10 percent Sc_2O_3 and 20 percent thorium oxide (ThO_2) for further treatment.

This crude fluoride cake was digested in a weak solution of sodium hydroxide for conversion to scandium hydroxide and was filtered to remove soluble sodium fluoride and other impurities. The hydroxide cake was digested with hydrochloric acid, and the pH was adjusted to precipitate thorium, titanium, zirconium, iron, and silica by hydrolysis. Filtration removed the contaminants, leaving a filtrate containing scandium and some iron and uranium, which was treated with oxalic acid to precipitate scandium oxalate. Iron and uranium were removed by filtration. The scandium oxalate precipitate was calcined to form scandium oxide and then dissolved in HCl for subsequent solvent extraction and stripping operations. Ammonia was used to precipitate scandium hydroxide and the hydroxide was calcined to 99.5+ percent scandium oxide.

Methods to extract scandium from thortveitite have been described (*4*, *7*). Dissolution with concentrated hydrochloric or sulfuric acids yields a gelatinous residue of silica which occludes appreciable scandium. To avoid this, one method is to roast the finely ground mineral with charcoal at 1,800° C to form scandium carbide, which can be decomposed by dilute hydrochloric acid. Another method consists of chlorinating in the presence of carbon at 850° C to produce soluble scandium chloride which is extracted by leaching. Scandium chloride does not sublime below about 970° C.

Ammonium oxalate or tartrate is added to the acid solution obtained after separation from silica by either of the above methods, precipitating the scandium, yttrium, and rare-earth elements as oxalates or tartrates. The filtered and washed precipitate is decomposed by igniting at 900° C and forms an impure scandium oxide, which is again dissolved in hydrochloric acid. Further purification of the scandium is by ion exchange or solvent extraction.

Scandium metal may be prepared from the oxide by converting it to scandium fluoride, heating it in a stream of hydrogen fluoride gas, and reducing scandium fluoride with calcium (*1*).

Very little data are available on the alloying of scandium with other metals.

USES

Scandium and its compounds have been used in research and development to obtain better understanding of the properties of these materials. Very few commercial applications have developed, the principal use for scandium being in radioisotope tracers for applications in oil well drilling and in analytical work.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS AND ALTERNATE MATERIALS

Scandium is currently a byproduct in uranium-processing.

For all uses for scandium thus far developed,

there are other cheaper and more abundant materials available.

RESERVES

Reserves of scandium are not known, but recent research points to the existence of relatively large quantities of scandium in uranium ores and even larger quantities in phosphate rock deposits.

Uranium ores usually contain less than 0.0005 percent scandium, but in view of the large reserve of uranium ore, 60 million tons in the United States and perhaps 600 million tons in the free world, the scandium content is quite large.

Recent studies on recovering scandium from fertilizer plant phosphoric acids revealed them to contain up to 0.002 percent scandium. Based on the resources of 16 billion tons of P_2O_5 in the United States and 48 billion tons in the world, phosphate deposits conceivably contain hundreds of thousands of tons of scandium.

Recovery of scandium from uranium ore or phosphate rock would be limited by the rate at which these ores were mined, and percentage recovery would be low because of the very low scandium content.

SOURCES OF STATISTICAL INFORMATION

Statistical data on scandium metal and compounds are obtained by the Bureau of Mines through annual canvassing, but most of the data are withheld to avoid disclosing company confidential information.

PRODUCTION, CONSUMPTION, AND TRADE

A pound of scandium produced in 1959 for research purposes was probably the largest quantity of scandium ever to exist in one place.

Sales of scandium oxide in 1962 were less than 30 pounds.

Data on imports and exports of scandium and its compounds are not available.

PRICES

The following prices for scandium and scandium oxide were quoted in 1964:

Item	1–99 grams, per gram	100 to 453 grams, per gram	1 to 2 pounds, per pound
Scandium metal:			
99 percent	$15.70	$13.50	$5,123
99.9 percent	16.60	14.25	5,393
Scandium oxide:			
99 percent	5.35	4.37	1,520
99.9 percent	5.63	4.60	1,600

Source: Research Chemicals, Division of Nuclear Corporation of America, Phoenix, Ariz.

RESEARCH

Government and industry have studied scandium in recent years, concentrating on extraction, determination of properties, fabrication, and development of uses.

Bureau of Mines research on scandium in recent years has consisted of studies of scandium resources and recovery methods (*5*, *6*), and thermodynamic properties.

OUTLOOK

Scandium probably will continue to be produced commercially for research and development purposes from uranium mill wastes. Once the pattern of uses develops, the supply may come from cheaper source materials such as the phosphate fertilizer industry.

Research and development of scandium will be continued on a small scale, and most of the expense will be borne by private concerns interested in the development of scandium.

Uses for scandium will probably develop slowly.

PROBLEMS

Problems confronting scandium extend from ore discovery through extraction, fabrication, high prices, and uses, the most acute problem being the almost complete absence of applications.

Though scandium is known to be widely dispersed in deposits of uranium, phosphate, and other minerals, information is lacking on the nature and extent of scandium in specific deposits for economical extraction. Therefore, all scandium concentrations discovered in ores, minerals, and residues from mills, smelter, and chemical operations become potential commercial sources.

Cheap and simple methods are needed for recovering scandium from uranium plant raffinates and residues as well as from phosphate ores and other source materials, because high

extraction costs cause high prices and discourage the development of uses.

More complete data on the physical, chemical, and metallurgical properties of scandium alloys and compounds are needed, because the special properties may determine new or potential uses. New alloy systems particularly need to be developed.

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SELENIUM

By Arnold M. Lansche [1]

SELENIUM production is centered at the electrolytic copper refineries in the industrialized nations. The element is widely distributed in the earth's crust but in small quantities, similar to gold. Native occurrences are rare, and there are no known areas of concentration that can be mined profitably for selenium alone under present technology.

The five selenium-producing companies in the United States accounted for 44 percent (928,000 pounds) of the free world's output in 1963. Canada, Japan, and the United States are the three major producers of selenium; the United States consumes about half of the free world's supply.

The most serious problem confronting the selenium industry is its dependence on electrolytic copper refinery production. This byproduct source is too inflexible to permit adjustment to shifting demand.

BACKGROUND

Selenium was discovered by Berzelius in 1817. He named the element after Selene, Greek goddess of the moon. Although useful applications of some of its properties were recognized as early as 1873, there were no large-scale uses for the element until about World War I.

Commercial production of selenium in the United States began in 1910 with the production of 10,000 pounds. Between World War I and World War II, the limited requirements for selenium could not absorb the quantity of selenium-bearing anode slimes generated at electrolytic copper refineries, and large quantities of slimes were stockpiled. About 1949, increased demand overtook the supply and stocks of anode slimes which had accumulated over many years were rapidly used.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Selenium is produced as a byproduct from the electrolytic copper refineries. U.S. companies reporting selenium production during 1963 were American Metal Climax, Inc., Carteret, N.J.; American Smelting & Refining Co., Baltimore, Md.; International Smelting & Refining Co., Perth Amboy, N.J.; Kawecki Chemical Co., Boyertown, Pa.; and Kennecott Copper Corp., Magna, Utah.

[1] Commodity specialist.

Primary production of selenium accounts for over 99 percent of the total domestic output. Although selenium is about equally abundant in the sulfide minerals of several metals, copper sulfide is the principal source; lesser quantities are recovered from lead smelter flue dusts treated at copper refineries and from selenium-bearing sulfur residues from chemical plants.

The geographic distribution of the free world selenium industry closely follows the pattern of the world's electrolytic copper refineries. Selenium is also a byproduct of lead smelting. Canada, Japan, and the United States are the three major producers of selenium, producing about 82 percent of the 1963 output. Other producers are Australia, Belgium-Luxembourg, Finland, Mexico, Northern Rhodesia, Peru, and Sweden, as well as U.S.S.R. and possibly other Communist nations.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Selenium may behave as either a metal or a nonmetal and occurs in several allotropic forms. It may be amorphous or crystalline. It can conduct electricity or act as an insulator and displays unipolar conductance of electricity.

High-purity selenium for electronic applications is marketed as pellets, sticks, and rectifier shot and contains from 99.95 to 99.99+ percent selenium. Material with 99,999+ percent selenium is available in pellets. Commercial-grade

selenium usually is marketed as a powder containing from 97.00 to 99.94 percent selenium. Government specifications for selenium for the strategic stockpile require that the commercial-grade selenium be not less than 99.0 percent selenium in the form of a black powder that will pass through a standard 200-mesh screen. Ferroselenium is used in the steel industry and contains 50 to 58 percent selenium. Selenium dioxide contains approximately 71 percent selenium and is sold in chemically pure and commercially pure qualities.

The poisonous characteristics of selenium compounds require careful handling. The maximum allowable concentration in air is about 0.10 parts per million (ppm). Contact dermatitis is caused by selenium salts. Selenium and the vapors of selenium, whether taken orally, inhaled as vapors, or absorbed through the skin, produce gastrointestinal disturbances and have deleterious effects upon the lungs, liver, and other organs. In acute stages the breath acquires a garlic odor. Contact with metallic or amorphous selenium has not been reported as a source of skin injury.

Selenium is required for the growth of some plants, is tolerated by others, and is deleterious to many. Animals native to seleniferous areas instinctively avoid forage containing large quantities of the element. Grazing animals not native to the seleniferous areas may eat the vegetation and sicken and die. Many times in the past when sheep, cattle, horses, or mules were driven or used in areas of selenium vegetation they would mysteriously become ill and die. It was not until about 1930 that the selenium content of plants was found to be the poisonous agent.

TECHNOLOGY

Selenium is widely but sparsely disseminated throughout the earth's crust, averaging approximately 0.09 ppm, and is 40th in abundance among the elements. It is rarely native and is not known to occur in sufficient quantities to make its extraction alone profitable. There is a wide range of selenium-bearing minerals that may become important as new exploitation techniques are developed. Selenium is associated with iron, copper, uranium, and other metals, and the most common sources are pyrite, chalcopyrite, bornite, and other sulfide minerals. After weathering, much of the selenium is released from these minerals; it may be redeposited as ferric selenite with secondary iron minerals such as limonite, or it may remain as native selenium. Small quantities find their way into the soil and, being soluble, are absorbed by certain plants.

In smelting copper ores, part of the contained selenium reports with the blister copper and part is carried through the flues as fumes and dust and is collected and returned to the reverberatory furnaces. To this circulating load of flue dust returning to the furnaces is added dust from lead smelters. Blister copper averages only about 0.05 percent selenium.

Selenium may be precipitated from a solution of selenosulfates by sulfur dioxide or from selenides by aeration of the solution. These properties are fundamental to the methods used to obtain selenium from its chief source—anode slimes from copper refineries. The copper and lead ores that contribute selenium to the anode slimes also contain tellurium and other impurities. As a consequence, each producer bases his extractive process on his experience, the raw material he must treat, and the product he sells.

All commercial processes may be considered as modifications or combinations of three fundamental methods: Smelting with soda ash, roasting with soda ash, and roasting with sulfuric acid. In the first two methods the selenium in the anode slimes is converted to sodium selenate which is soluble in water. Tellurium is precipitated from the solution by neutralization with acid and recovered by filtration, and then elemental selenium is precipitated with sulfur dioxide. In the third process, the anode slimes are roasted with sulfuric acid. Selenium dioxide volatilizes and is recovered in a wet Cottrell precipitator, leaving copper and other metals behind as sulfates.

High-purity selenium is made by several methods, such as fractional distillation, zone refining, dissolving as selenious acid followed by purification with subsequent reduction to selenium, and catalytic oxidation to high-purity selenium dioxide followed by either gaseous or wet reduction.

USES

Selenium has a wide range of applications, but most require only small quantities of metal. Nearly all of selenium consumption is in the electronic, chemical, glass, and metallurgical industries.

The electronic and electrical industries have become the major users of selenium during recent years. Of the selenium employed in these fields, over 90 percent is applied in manufacturing dry plate metal rectifiers, while most of the remainder is used in photoelectric cells. Selenium rectifiers have been known since 1884, and have been used commercially since about 1930. Selenium rectifiers change alternating to direct current and are extensively used in electroplat-

ing, welding, direct-current motor operation, battery chargers, magnet coils, arc lamps, induction braking, and voltage regulators.

Selenium photoelectric cells are used in photographic exposure meters, detectors, electric eyes, colorimeters, and pyrometers. Selenium is used in thermoelectric devices and other electronic applications using semiconductor materials.

The chemical industry consumes nearly one-third of the total selenium, principally in pigment manufacture. Selenium is compounded with cadmium sulfide in manufacturing the orange-red-maroon range of cadmium-selenium pigments. These give strong, bright colors with good light stability and resistance to heat and chemical attack. Selenium pigments are used to color many products, including plastics, paints, enamels, inks, and rubber. Selenium is used as a catalyst in the pharmaceutical industry. It has been applied in producing cortisone and niacin. Selenium is also used as a fungicide for control of dandruff and dermatitis and in manufacture of deodorant pharmaceuticals. The rubber industry uses selenium, mostly in the form of selenium diethyldithiocarbonate. The selenium acts as an accelerator and vulcanizing agent. It also promotes resistance to heat, oxidation, and abrasion and increases the resilience of the rubber. Selenium and its compounds are widely employed in industrial and research chemistry. Selenium dioxide oxidizes organic compounds and can be either a hydrogenating or a dehydrogenating agent. Selenium is a hydrogenation and cracking catalyst in crude oil and coal distillations. Soaps, waxes, edible fats, and plastics are produced by fat hardening with a selenium catalyst. Selenium imparts exceptional antioxidant properties to printing ink, mineral oils, transformer oils, and vegetable oils. Nondrying properties of linseed, oiticica, and tung oils are due to selenium. Selenium also retards gelation in tung oil. The antioxidant and antigalling properties of selenium compounds find application in lubricating oils and in extreme-pressure lubricants. Selenium compounds are finding application as insecticides, parasiticides, bactericides, and herbicides. Photographic photosensitizers and toning baths contain selenium compounds such as sodium selenosulfate. Mercury vapor detectors, fireproofing agents, insect repellants, phosphorescents, and luminescents have been made from selenium compounds.

Selenium is important to the glass industry to eliminate the greenish tinge in glass caused by iron impurities. From 0.02 to 0.3 pound of elemental selenium, sodium selenate, barium selenite, or sodium selenite per ton of glass is required; the exact quantity is determined by the iron content to be neutralized. Excess selenium causes a pink tinge, which is desirable in milk bottles and a few other food containers. From 1 to 50 pounds of selenium per ton of glass yields a desirable ruby-red glass, which is used in tableware, vehicular taillights, traffic and other signal lenses, light filters, and infrared equipment.

Selenium is used to control porosity in stainless-steel castings and to improve the machinability without reducing corrosion resistance or the hot-forging and cold-working properties. Selenious acid is used in the steel industry as an etchant. The addition of selenium improves the machinability of copper and copper-base alloys.

Xerography, a dry photographic process, employs selenium-coated metal disks from which the photographic image is transferred by static electricity. Radioactive selenium has been utilized in radiography. The oxychloride is a powerful solvent; it may be used as a paint and varnish remover and as a solvent for rubber resins, glue, and other organic substances.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Selenium is primarily a byproduct of the electrolytic refining of copper. The electrolytic slime from which selenium is extracted also contains gold, lead, silver, and tellurium as recoverable coproducts. Selenium is a byproduct of lead smelting and occurs in some sulfur residues generated at chemical plants.

ALTERNATE MATERIALS

There are satisfactory substitutes for selenium in many of its applications. The chief substitutes are germanium and silicon in electronic applications, and sulfur and tellurium in the chemical, rubber, and steel industries.

The high price and shortage during 1950–57 encouraged selenium consumers to find substitutes. Substitutes subsequently made competitive inroads into the major consuming segments of the selenium industry.

SECONDARY SOURCES AND RECOVERY

Secondary selenium is reclaimed from factory scrap generated during manufacture of selenium rectifiers, from burned-out rectifiers, and from spent catalysts. Selenium in the chemical industry is mostly expendable. There was no reported recovery of selenium from secondary sources in 1962 and 1963.

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RESERVES

Selenium reserves are primarily a function of copper and, to a lesser extent, lead reserves. The recoverable reserve of selenium in domestic copper ores is about 25 million pounds, based on the present recovery rate of three-fourths pound of selenium per ton of copper treated. About 4 million pounds of selenium is contained in lead ore reserves. Large tonnages of selenium are contained in the rock strata and soils of the Western United States.

SOURCES OF STATISTICAL INFORMATION

Statistics on selenium production, shipments, and stocks are received quarterly and annually by the Bureau of Mines from producers of selenium and selenium compounds. These data are received on a company confidential basis, and individual company data are combined to make up the published totals. Five companies supplied statistics in 1963. World production data also are compiled by the Bureau. Imports of selenium are available from records of the Bureau of the Census, U.S. Department of Commerce.

PRODUCTION, CONSUMPTION, AND TRADE

Production and consumption of selenium in the United States were about the same during 1959–63. In 1959 and 1960 consumption exceeded production plus imports, but in 1961–63 the opposite was true. Producer stocks were adequate to supply the deficit in 1959 and 1960. Output was 728,000 pounds in 1959 compared with 928,000 pounds in 1963, and reached the high level of 1,022,000 pounds in 1961.

Canada was the source of most of the selenium imported by the United States in 1959–63. In 1963 Canada supplied about 250,000 pounds, or 74 percent of the total selenium imports. Selenium comes sporadically from Belgium-Luxembourg, Japan, Norway, Peru, Sweden, the United Kingdom, and West Germany. Selenium-bearing residues have been received occasionally from Northern Rhodesia. Imports from Mexico are reported as "lead flue dust—selenium content." Ultimately, the selenium content of the lead flue dusts is included and reported as domestic selenium production.

Tariff rates of 20 and 25 percent, respectively, were levied on selenium and selenium salts in 1909 and removed in 1913. Since that time all selenium has remained free of tariff.

STRATEGIC CONSIDERATIONS

The United States has an adequate supply of domestic selenium. A stable domestic copper industry, plus substantial quantities of selenium available from Canada and Mexico, should eliminate any possibilities of a serious selenium shortage under foreseeable conditions. While a stable copper production assures selenium self-sufficiency, at the current rate of consumption this tie-in to copper production precludes rapid expansion if an unexpected increase in demand or strategic use should develop.

From the standpoint of strategic consideration, the major part of the selenium recovery industry is vulnerably concentrated in a relatively small area in Maryland, New Jersey, and eastern Pennsylvania. One producer is in Utah.

The Office of Emergency Planning raised the selenium stockpile objective to 475,000 pounds on April 17, 1964. On June 30, 1964, the inventory of Government-owned selenium metal totaled 439,800 pounds, 92.6 percent of the maximum stockpile objective. Of the total stocks, 97,100 pounds was in the national (strategic) stockpile, 110,500 in Commodity Credit Corporation stocks, and 232,200 in the supplemental stockpile.

Selenium was placed in group B of the "Strategic and Critical Materials List" in September 1948, and in May 1953 it was transferred to group I.

The Office of Defense Mobilization established an expansion goal (No. 178) on October 9, 1952, for a total supply of 1.1 million pounds of selenium in 1955, including scrap recovery and imports. This goal was revised on September 29, 1955, to a supply of 1.2 million pounds annually from domestic primary sources, exclusive of scrap recovery and imports. The expansion goal was closed on February 28, 1957.

GOVERNMENT PROGRAMS

A critical supply shortage for selenium began during 1950. On December 10, 1951, the National Production Authority issued Order M–91 placing both imported and domestically produced selenium under complete allocation. The order became effective in February 1952 and was revoked in February 1953.

Exportation of selenium was under Government control and limited to approximately 24,000 pounds annually from 1953 through 1956. This was changed May 2, 1957, to allow industry to export unlimited quantities of material to friendly countries. However, exporters were required to obtain a license through the U.S. Department of Commerce for all shipments.

Selenium was designated by the President as eligible for acquisition under the 1959 and 1960 barter program of the U.S. Department of Agriculture, Commodity Credit Corporation (CCC). In 1961 and 1962 it was left out of the barter program. On February 13, 1963, the Department of Agriculture revised the program and U.S. firms were invited to submit offers for commercial-grade selenium produced from raw materials originating in friendly foreign countries, in exchange for CCC-owned agricultural commodities for export to CCC-approved destinations.

Selenium is eligible for financial assistance of up to 50 percent of the cost of exploration projects approved by the Office of Minerals Exploration (OME).

PRICES

In 1959–63 the price of selenium declined steadily. The high for the commercial-grade powder was $7 per pound in 1959; other prices were $6.50 to $7 in 1960, $5.75 to $6.25 in 1961, and $5.75 to $6.25 in 1962. In 1963 the range was $4.50 to $5.75, with the price at $4.50 for most of the year. The high-purity grade was $9.50 per pound in 1959, and at the end of 1963 the price was $6. In 1963 99.999 percent selenium sold for $13 to $20 per pound.

Selenium is not paid for by the custom copper refiner.

TAXES

There are no special taxes on selenium. Producers are granted a depletion allowance of 15 percent on domestic and foreign production.

TRANSPORTATION

Commercial-grade and high-purity selenium are shipped in polyethylene bags, 30 pounds to a carton, with four cartons stacked within a larger carton to make a 120-pound unit. Ferroselenium usually is packed in wood barrels of 500 pounds each; smaller quantities are shipped in wood boxes. There are no shipping regulations for selenium metal or its compounds.

RESEARCH

Selenium purification research was reported by the Royal Radar Establishment, Great Malvern, England (*6*).[2] Reports on biological applications of selenium compounds were made by government agricultural agencies in New Zealand (*2*, *3*, *5*).

Industry continued to do research on the use of selenium in alloy steels to improve their machineability (*4*). Metal selenides were studied in industry laboratories for their applicability as lubricants (*1*).

OUTLOOK

The variety of properties displayed by selenium assure its continued use in many areas of industry and for the protection of animal life. A steady growth can be expected in conventional uses, especially in the steel, chemical, glass, ceramic, drug, and electrical industries.

The short-term outlook indicates, however, that the selenium industry cannot grow beyond the limit imposed on it by the copper and lead industries unless alternate sources of selenium on an economic and commercial scale are found. The inducement of a higher price was not successful in efforts to find these alternate sources of supply, and it is unlikely that supply, other than as a byproduct, will be developed.

PROBLEMS

The major problem facing selenium producers is the inability to maintain a supply-demand balance. The principal reason for the failure to establish market stability stems from the metal's byproduct relationship with the copper-refining industry. This relationship creates a problem of inflexible procurement because production cannot be adjusted to requirements.

Although the chemical and physical properties of selenium have been extensively studied and fully covered in the literature, there remain numerous unsolved problems of application to potential new uses. Problems resulting from the increased use of the high-purity selenium and its handling and storage are especially significant.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

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SILICON

By John L. Morning [1]

SILICON is featured by its unlimited supply position and its diversity of forms and uses. A recent development of substantial importance has been its use in achieving miniaturization of electronic circuits and devices. Silicon metal and silicon alloy's largest industrial use is as an alloying agent in iron and steel products and in aluminum alloys.

Silicon as covered by this chapter includes high-purity silicon for semiconductors, silicon metal and silicon alloys for chemical and metallurgical applications, and specialty silicon products such as silicon carbide and silicon nitride. Additional information on silicon alloys will be found in the Ferroalloy chapter in this bulletin.

The growth in demand for silicon alloys as an addition agent to steel has paralleled that of the steel industry since 1889 when R. A. Hadfield discovered silicon steels. Since the turn of the century, advancing technology has introduced metallurgical-grade silicon metal, special grades of silicon alloys, silicone products, and high-purity silicon.

High-purity silicon is used in electronic applications and is produced by six firms. Metallurgical-grade silicon metal and silicon alloys are made by 13 metallurgical firms for use as addition agents in ferrous and nonferrous industries along with some use in chemical applications.

High-purity silicon is produced to customers' specifications in polycrystalline or single crystal form. Silicon metal is manufactured in numerous grades according to chemical specifications for the metallurgical and chemical industries.

Silicon in its various forms is used in chemical, metallurgical, electrical, electronic, refractory, optical, and abrasive applications. Semiconductor devices made from silicon are being used where high reliability is required. Ferrosilicon is the most important deoxidizer of steel and is also an important alloying agent. Metallurgical silicon metal is the starting material for making silicone products and is used as an alloying agent in aluminum, copper, and nickel alloys.

Shipments of high-purity silicon to the electronics industry in 1963 was 24,539 kilograms of polycrystal and 5,917 kilograms of single crystal. Consumption of silicon metal, ferrosilicon, and other silicon alloys totaled 651,628 short tons.

High-purity silicon is priced according to customer's specifications as to doping, resistivity, and size. Polycrystalline silicon, without dopant, is priced at $123 per kilogram in quantity lots. Silicon metal for metallurgical and chemical use ranges from 16.75 to 21.50 cents per pound.

Application research is being sponsored by the U.S. Government, but most research is being performed by private industry. Integrated circuitry and miniaturization of devices have evolved from these efforts.

The outlook is good for the continued growth of semiconductor silicon for electronic applications. With the trend to miniaturization in devices it is probable that primary production of high-purity silicon will not rise markedly.

A major problem for the high-purity silicon producer is the changing technology which may outdate his process or product as a result of new developments.

BACKGROUND

Progress in producing and using silicon and its compounds was slow until well into the 20th century. Berzelius, in 1824, prepared the first relatively pure silicon by passing silicon tetrachloride over heated potassium. The first crystalline silicon was made by Deville in 1854. A major advance in technology was made in 1889

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when R. A. Hadfield published the results of his comprehensive investigation of the effects of silicon in steel and the discovery of silicon steels.

Once the demand for silicon was created, production of ferrosilicon in the newly developed electric furnace was initiated in the 1890's by J. T. Moorehead and du Chalmot of the Willson Aluminum Co., at Spray, N.C., and later at Holcomb Rock, Va., and Glen Ferris, W. Va. In 1891, E. G. Acheson discovered how to make the abrasive, silicon carbide, and the same year founded the Carborundum Co. Patents for making metallurgical-grade silicon metal were first issued to H. N. Potter in 1907. F. M. Becket patented in 1921 an acid purification means for preparing silicon that was more than 99 percent pure. In 1949, technologists for E. I. du Pont de Nemours & Co., Inc., headed by D. W. Lyon produced the first grade of silicon suitable for transistors and other semiconductor devices by reducing the tetrachloride with zinc. During the first half of the 20th century silicon was being introduced into alloys of aluminum and nickel, and as a starting material for manufacture of silicones.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Primary producers of high-purity silicon at the close of 1963 were:

Company:	*Location*
Allegheny Electronic Chemicals Co.	Lewis Run, Pa.
Dow Corning Corp.	Hemlock, Mich.
Linde Co. (Div. of Union Carbide Corp.).	Cleveland, Ohio
Mallinckrodt Chemical Works	St. Louis, Mo.
Monsanto Chemical Corp.	St. Charles, Mo.
Texas Instruments, Inc.	Dallas, Tex.

Since 1960, six firms have ceased production of high-purity silicon due to changing technology and declining profit in a saturated market.

In 1963, 13 firms made silicon metal, ferrosilicon (including silvery iron) or other silicon alloys in 27 plants. A list of producers of silicon metal and silicon alloys is included in table 1 of the Ferroalloy chapter in this bulletin. Production of silicon metal and silicon alloys for metallurgical use in 1963 was 696,000 tons.

DEFINITION OF TERMS, GRADES, SPECIFICATIONS, AND PROPERTIES

Elemental silicon is a light, brittle substance, dark gray in color with a metallic luster. Structurally, silicon has the same cubic symmetry as diamond and four valance electrons. Its atomic weight of 28.09 and density of 2.33 g/cm^3 are less than half those of germanium. Currently accepted electronic, mechanical, and thermal properties comparing silicon and germanium have been published (*8*).[2]

In high-purity silicon technology, the term "semiconductor" is used to designate a class of material. It is a material that has an electrical conductivity intermediate between a conductor and an insulator. Silicon is a monatomic semiconductor along with germanium, gray tin, and diamond. Actually silicon is an imperfect insulator and will not serve satisfactorily as a semiconductor until it has been purified and then had precise amounts of specific impurities added. This technique is called doping.

High-purity silicon is produced in polycrystalline form and converted to single crystal by float-zone or crystal-pull (Czochralski) methods of refining. High-purity silicon is marketed in polycrystalline form either as rods or chunks for customers to process, or as single-crystal rods, slices or wafers depending on customer requirements. Producers supply high-purity silicon to a resistivity specification as measured in ohm-centimeters and conductivity type, positive or negative (p or n).

Silicon metal is marketed to the metallurgical and chemical industries in numerous grades depending principally on iron, aluminum, or calcium specifications. Five typical grades of metallurigcal silicon metal are shown in table 1. Most grades can be purchased with 0.03 percent maximum calcium specification.

TABLE 1.—*Grades of silicon metal of metallurgical quality*

[Percent]

Grade	Silicon minimum	Iron maximum	Calcium maximum	Aluminum maximum
Maximum 0.35 percent iron	98.40	0.35	0.07	----------
Maximum 1.00 percent iron	98.00	1.00	.07	----------
Low calcium	98.00	1.00	.03	----------
High calcium	97.50	1.00	.40	----------
Low aluminum	98.50	1.00	.03	0.10

Silicon alloys include ferrosilicon, silvery pig iron, silicomanganese, ferroaluminum-silicon, magnesium-ferrosilicon, ferrochrome-silicon, ferromanganese-silicon, calcium-silicon, calcium-manganese-silicon, barium-silicon, ferrozirconium-silicon, and zirconium-silicon, all of which are principally used in metallurgical industries. Ferrosilicon accounts for the largest tonnage of the silicon alloys produced. The

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

American Society for Testing and Materials (ASTM) lists tentative standards for five of these products (*2*).

Silica (SiO_2) for metallurgical use in producing silicon metal, ferrosilicon, and other silicon alloys is usually quartz, quartzite, or well-cemented sandstone with at least 98 percent silica content. Size requirement ranges between 1 and 6 inches depending on the type of reduction furnace used in the manufacturing process. Impurities such as lime, magnesium, and aluminum are kept low to reduce the slag volume to a minimum. Arsenic and phosphorus are objectionable because unstable compounds are formed which cause deterioration and disintegration of the finished product.

Silicon carbide manufacture uses a high-grade glass sand with a silica content of at least 99 percent. Like silica for silicon metal products, impurities such as lime, magnesium, phosphorus, and arsenic must be low. The sand should be dust free and between 35 mesh and 150 mesh.

Silica ores are used in metallurgical processes as a fluxing material in nonferrous metal and phosphorus smelting. Individual companies use their own specifications for this material as price is more of a factor than quality.

TECHNOLOGY

The technology of making and fabricating high-purity silicon has changed rapidly since Du Pont developed a process for making hyperpure silicon by the reduction of silicon tetrachloride ($SiCl_4$) with zinc (*14*). The first commercial production by this process was in 1951. From 1951 to 1960, producers were concerned in making improvements in starting materials and in their intermediate and final products, while device makers were making improvements in the fabrication and application of these materials. Boron was the main obstacle in this period, since no method of purifying silicon could remove this element including zone refining, which is the standard method of reducing boron in germanium. By 1960, due to change in processes boron had ceased to be a problem.

The starting materials for high-purity silicon are metallurgical-grade silicon metal and chlorine which are reacted in a shaft or fluidized bed reactor to form liquid silicon tetrachloride, or by the addition of hydrogen to the reactor to form trichlorosilane ($SiHCl_3$). These products are generally purified by the use of cold traps, absorption techniques, or distillation in quartz columns.

In 1959, device manufacturers experimented with crystal growth by vapor phase deposition techniques called thin film or epitaxial deposition. Most producers and all device makers are now using some form of this method either for supplying material to device makers for assembly or in creating devices. The common feature in depositing silicon epitaxially from the vapor phase is a hot-silicon single crystal wafer or substrate exposed to an atmosphere charged with a silicon compound such as silicon tetrachloride or trichlorosilane. The substrate is heated to between 1,000° and 1,300° C depending upon the silicon compound being used. The substrate should have a smooth, clean, structureless surface prior to deposition of the thin film. One method to achieve this is to etch the substrate while at temperature with hydrogen chloride gas. The growth rates of thin films deposited on substrates range from 0.1 to 3 microns per minute (*4*, *5*, *13*, *18*, *19*).

An advancement in technology was made by the introduction of semiconductor silicon that has low oxygen and low etch pit density made by a new undisclosed process. Low oxygen is typical of single crystal material produced by float zoning and low etch pit density is typical of single crystal rod made by the crystal-pull or Czochralski process. This new method of manufacture combines the best characteristics of both older techniques. In addition, this new type of silicon has a minority carrier lifetime of up to 8,000 microseconds, compared with normal specifications of 100 microseconds for conventional single crystal (*6*).

Domestic production of high-purity silicon is believed to be made by the hydrogen reduction of trichlorosilane or silicon tetrachloride using modified processes of Siemens or van Arkel. Producers that used processes such as decomposition of silicon tetraiodide (SiI_4), thermal cracking of Silane (SiH_4), and zinc reduction of silicon tetrachloride have dropped out of the market. Most producers keep their methods of manufacture secret, as proprietary, in this highly competitive business.

Japanese producers list reduction of silane and silicon tetrachloride, thermal decomposition of silane and trichloresilane, and hydrogen reduction of trichlorosilane and silicon tetrachloride as their methods of production of polycrystalline silicon (*11*).

Silicon solar electric cells have been made by diffusing thin layers of selected elements into silicon, usually boron and phosphorus. Device manufacturers continue to improve performance of these devices by switching from phosphorus and boron to aluminum for doping. The currently produced solar cells are more efficient than formerly with higher power outputs and resistance to radiation damage (*7*).

Recovery of silicon in the production of metallurgical silicon metal in the electric-arc furance has increased from 70 to about 90 percent with improved operations. At one time it was considered good furnace practice to hold production to a 2-percent iron specification. Today, large tonnages are produced to a maximum of 0.3 percent iron content. To meet customers requirements, low-aluminum or low-calcium grades have been developed. Methods of refining impure silicon metal to lower the content of these elements include treatment with oxidizing agents such as air, oxygen, carbon dioxide and chlorine. These refining agents vary in their ability to selectively remove calcium or aluminum and affect the yield of silicon in the refining operation (*12*).

The manufacturing processes for silicon metal and ferrosilicon are the same except for introduction of iron for the latter. Ferrosilicon is made by reducing quartz gravel, crushed quartzite, or well-cemented sandstone with coke, low-volatile coal or charcoal together with iron such as steel turnings, mill scale, or iron sinter in an electric arc furnace. To produce the various grades of ferrosilicons and silicon metals the charge is varied to give the desired product.

Substantial research has been done with 3 percent silicon-iron sheet on the orientation of the crystals in two directions for use in the cores of transformers and the armatures and stators of electric motors and generators. By orienting the crystals so that the magnetic flux flows along the edges of the cubic crystal, the cores are easier to magnetize and have the lowest energy loss. For many years transformer sheet has been grain-oriented in one direction, now with proper selection of processing cycles, silicon iron sheet with improved magnetic properties can be produced with cube orientation (*17*).

Silicon carbide (SiC) is manufactured in electric-resistance furnaces by the reaction of silica and carbon ($SiO_2+3C=SiC+2CO$) at a temperature above 1,500° C. Sawdust and salt are added to the charge, sawdust to promote porosity for the circulation of hot vapors, salt to react with iron and other impurities to produce volatile chlorides. The reduced product is cleaned, crushed, and ground to a particular size prior to making finished products such as heating elements, abrasives, high temperature refractories, and corrosion resistance hardware (*3*).

The British Admiralty has developed a new production process for silicon nitride (Si_3N_4) in which specially graded silicon powders are shaped into parts and sintered at 2,600° F in a nitrogen atmosphere. The process can be interrupted when the material is partially hardened, additional fabrication can be performed and the material given a final nitriding to complete the conversion. Silicon nitride produced by this process will withstand temperatures of 2,200° F in air or 3,000° F in inert atmospheres. Resistance to attack by molten metals up to 2,000° F and to extreme thermal shock are features of this material (*15*).

USES

High-purity silicon is used mainly where performance and reliability are more important than price. Silicon and germanium, the elements most commonly used in semiconductor devices, transistors, diodes, and rectifiers, perform the functions that a decade ago were done by vacuum tubes, or by selenium, copper oxide, or similar rectifiers. Silicon maintains its electronic characteristics to an operating temperature of 250° C, compared with 75° C for germanium.

Present development in miniaturization of devices is called "integrated circuitry." A small chip of silicon approximately one-eighth of an inch square can contain 2 electronic circuits with 15 transistors and 13 resistors. By combining such components together in one package, a reduction in lead wires, soldered joints, and number of containers eliminates many weak points of conventional circuitry.

Optical silicon, which is polycrystalline, is manufactured by several producers in shapes for covering infrared sensing devices used in aerospace instruments. Silicon will transmit more radiation from 1.2 to 6.7 microns at a higher temperature (350° C) and thicker sections than most materials.

Silicone manufacturers have become heavy users of silicon metal in the last decade. This industry is one of the chief users of the silicon metal made in electric furnaces by ferroalloy producers. It is crushed and ground to a powder, reacted with methyl chloride in the presence of copper and copper-oxide catalysts to produce a mixture of silanes which are separated by fractional distillation. From these are separated the chemicals, methyltrichlorosilane, dimethyldichlorosilane, and trimethylchlorosilane, from which some 450 silicone resins, lubricants, elastomers, antifoaming agents, and water-repellent compounds are made (*9*).

A minor use of silicon is as a drier, the familiar silica gel. Silica gel can be regenerated by heating for repeated use as a moisture absorbent.

Silicon nitride is used as a high-temperature oxidation-resistant coating for metals, as laboratory ware such as protection tubes and supports

subjected to extreme thermal shock and as furnace linings for some molten metals.

Silicon metal is used chiefly in the metallurgical industry for alloying with aluminum, copper, and nickel. Aluminum is alloyed with 2 to 25 percent silicon to improve casting fluidity, and at the higher percentages to improve both fluidity and wear resistance. Several elements including phosphorus are added in minor amounts to refine the silicon particle to improve the wear resistance and machinability of the higher alloys of silicon in aluminum. Copper alloys with silicon are strong, weldable, and have good resistance to corrosion and galling. Nickel with silicon possesses excellent tensile properties, and corrosion resistance to sulfuric acid.

Some ferrosilicon is used in the silicothermic process for making magnesium wherein the silicon constituent reduces magnesium oxide. Ferronickel is manufactured by the Ugine Process in electric arc furnaces using ferrosilicon as a reductant.

Ferrosilicon, including silvery pig iron, is primarily used in the iron and steel industry for the deoxidation of molten metal, as an alloying agent to meet chemical specifications, and in some instances for reduction of metalloids in the slag. The ferrosilicon most commonly used for these purposes contains 50 percent silicon and 50 percent iron; however, high-silicon specification steels such as electrical grades generally are made with higher percentage silicon content ferrosilicons.

Ferrosilicon is added to the furnace or ladle and occasionally to the ingot mold for deoxidation. More ferrosilicon is used as a deoxidizer than all other deoxidizing agents combined. Ferromanganese, which is used in larger tonnage than ferrosilicon, can act as a deoxidizer but is added to steel primarily for control of sulfur and to enhance certain physical properties.

Most ferrosilicon consumed to form an alloy with iron is used in electrical sheet steels of 0.5 to 5 percent silicon content. Smaller quantities are used in spring and high-temperature alloy steels. In cast irons, however, as much as 17 percent silicon is employed to resist growth and scaling at elevated temperatures, and corrosion of certain mineral acids, free chlorine and copper salt solutions (*1*, p. 518). In combination with magnesium, silicon gives a "plunging alloy" for making ductile, nodular iron.

Silicon imparts high strength to steel at moderately elevated temperatures. Shih, Averbach, and Cohen (*16*) show that silicon additions up to 1.5 percent in standard ternary alloy steels beneficially affect the mechanical properties by increasing the tensile and yield strengths and yet maintain the same ductility properties of the standard compositions. A comparison of mechanical properties of AISI (American Iron and Steel Institute) 4340 and 4340+(1.5 percent Si) steels hardened and tempered at 500° F for 1 hour are given in table 2 (*16*).

Another use of silicon is as a diffused case for steel parts for protection against corrosion, heat, and wear. The case is produced at 1,700° to 1,850° F in the presence of silicon and chlorine. The usual applications of siliconized parts are as automotive water pump shafts, and valve guides, valves and fittings in the chemical industry, and as furnace parts and fittings (*1*, pp. 708–709).

TABLE 2.—*Influence of silicon on an alloy steel*

Property	4340	4340 (1.5 percent silicon)
Hardness, Rockwell C	51	54.5
Tensile strength, pounds per square inch	260,000	300,000
Yield stress, do	230,000	256,000
Elongation, percent	6.7	6.3
Reduction of area, do	40	40
Room temperature Charpy impact strength, V-notch, foot-pounds	14.3	15.9

ALTERNATE MATERIALS

The principal alternate material for silicon in semiconductor applications is germanium. Germanium, however, breaks down electronically above 75° C while silicon can be used to 250° C. Newly developed semiconductor materials such as gallium arsenide and cadmium sulfide may replace high-purity silicon in certain applications.

Metals such as aluminum, manganese, and vanadium, nonmentals and compounds, can be substituted for ferrosilicon as deoxidizers but only at higher cost.

SOURCES OF STATISTICAL INFORMATION

The Bureau collects production and shipment information quarterly from producers of metallurgical silicon metal and silicon alloys, and consumption canvasses since January 1, 1959, have been conducted monthly combined with other ferroalloy commodities. High-purity silicon production and shipment information formerly obtained and published quarterly, are now obtained and published annually. The Bureau's statistics for single-crystal silicon do not include data for companies that do not produce polycrystal material. The data on imports and exports of silicon metal and silicon alloys are supplied to the Bureau of Mines by the Bureau of Census.

PRODUCTION, CONSUMPTION, AND TRADE

High-purity silicon production in 1963, as shown in table 3, was 41,247 kilograms, of which 34,582 kilograms was in the form of polycrystal. Shipments of 24,539 kilograms of polycrystal and 5,917 kilograms of single crystal had a combined estimated value of $11 million.

The high-purity silicon shipments went primarily to the electronics industry for fabrication into rectifiers, transistors, diode and complex electronic devices. Increase in the number of such fabricated siilcon products, in the face of lower production of high-purity silicon for 1963, reflected increased efficiency in fabrication of devices and changes in technology.

Salient statistics for 1963 for metallurgical silicon metal and principal silicon alloys are shown in tables 4 through 7. Silvery pig iron is used primarily in gray and malleable iron castings, the true ferrosilicons mainly in iron and steel production and metallurgical silicon metal primarily as an addition agent to aluminum base alloys but with substantial amounts being used by the growing silicone industry.

A change in classification of imports was effective August 31, 1963. Classifications of ferrosilicon grades are now over 8 percent but not over 60 percent silicon, over 60 percent but not over 80 percent silicon, over 80 percent but not over 90 percent silicon, and over 90 percent silicon. Classification of metallurgical silicon metal was specified as being not over 99.7 percent silicon; high-purity silicon, formerly lost in a blanket classification, will now be reported as silicon metal containing over 99.7 percent silicon.

Tariffs for most nations effective in 1964 were as follows: Silicon containing by weight not over 99.7 percent of silicon was 4 cents per pound contained silicon. Silicon containing by weight over 99.7 percent of silicon was 10.5 percent ad valorem. Duty rates for Communist nations were as follows: silicon containing by weight not over 99.7 percent of silicon—8 cents per pound contained silicon and silicon containing by weight over 99.7 percent silicon—25 percent ad valorem.

Tariffs for ferrosilicon products are listed in table 8 of the Ferroalloy chapter in this bulletin.

TABLE 3.—*Production, shipments, and value of high-purity silicon in the United States*

Type	1962			1963		
	Production (kilograms)	Shipments		Production (kilograms)	Shipments	
		Quantity (kilograms)	Value (thousands)		Quantity (kilograms)	Value (thousands)
Polycrystal	36, 902	37, 046	$4, 922	34, 582	24, 539	$3, 041
Single crystal: [1]						
Negative:						
Rods	5, 932	5, 139	5, 288	3, 758	3, 027	3, 098
Slices [2]	2, 117	2, 104	4, 008	1, 651	1, 656	3, 529
Total	8, 049	7, 243	9, 296	5, 409	4, 683	6, 627
Positive:						
Rods	990	(3)	1, 387	485	547	544
Slices [2]	582	(3)	905	771	687	953
Total	1, 572	1, 600	2, 292	1, 256	1, 234	1, 497
Total single crystal	9, 621	8, 843	11, 588	6, 665	5, 917	8, 124

[1] Does not include data for companies producing single-crystal high-purity silicon solely from scrap and other secondary and purchased polycrystal.
[2] Includes epitaxial wafers.
[3] Figure withheld to avoid disclosing individual company confidential data.

TABLE 4.—*Net production and shipments of silvery pig iron, ferrosilicon, and silicon metal in 1963*

[Short tons, gross weight]

Alloy and percent of silicon contained	Net production	Shipments
Silvery pig iron:		
Blast furnace: 5–13	63, 908	70, 975
Electric furnace: 14–20	132, 545	133, 090
Ferrosilicon:		
21–55	276, 256	285, 765
56–70	20, 922	22, 172
71–80	63, 646	63, 415
81–89	14, 288	14, 635
90–95	1, 944	2, 302
Silicon metal: 96–99	64, 574	65, 005
Ferrosilicon briquets: 40–50	45, 704	45, 366
Miscellaneous silicon alloys	12, 276	13, 219
Total	696, 063	715, 944

TABLE 5.—*Consumption by major end uses, and stocks, of silicon alloys in the United States in 1963*

[Short tons, gross weight]

Alloy and percent of silicon contained	Stainless steels	Other alloy steels [1]	Carbon steels	Tool steels	Steel mill rolls	Gray and malleable castings
Silvery pig iron:						
5–13	1	731	731	----------	775	85, 970
14–20	1	6, 571	19, 258	----------	114	99, 668
Ferrosilicon:						
21–55 [3]	6, 710	53, 783	85, 469	815	914	71, 527
56–70	401	5, 468	13, 941	----------	----------	822
71–80	8, 297	11, 148	5, 722	445	215	11, 294
81–89	106	804	2, 165	----------	137	4, 307
90–95	25	1, 226	168	----------	45	277
Silicon metal: 96–99	11	120	55	10	----------	419
Ferrosilicon briquets: 40–50	----------	144	320	----------	17	32, 426
Miscellaneous silicon alloys [6]	277	6, 025	5, 260	54	128	14, 228
Total	15, 829	86, 020	133, 089	1, 324	2, 345	320, 938

Alloy and percent of silicon contained	Aluminum base alloys	High temperature alloys	Other alloys	Miscellaneous uses	Total consumption	Stocks Dec. 31, 1963
Silvery pig iron:						
5–13	----------	----------	1	1, 771	89, 980	6, 588
14–20	----------	----------	51	[2] 6, 437	132, 100	12, 643
Ferrosilicon:						
21–55 [3]	44	189	2, 410	[4] 16, 941	238, 802	19, 366
56–70	----------	----------	----------	[4] 4, 167	24, 799	1, 128
71–80	----------	22	32	11, 014	48, 189	4, 386
81–89	----------	----------	18	11	7, 548	938
90–95	2, 563	----------	61	7	4, 372	418
Silicon metal: 96–99	32, 913	568	734	[5] 7, 946	42, 776	2, 071
Ferrosilicon briquets: 40–50	----------	----------	----------	4	32, 911	3, 412
Miscellaneous silicon alloys [6]	107	68	53	3, 951	30, 151	2, 279
Total	35, 627	847	3, 360	52, 249	651, 628	53, 229

[1] Includes quantities of carbon steels because some firms failed to specify individual uses.
[2] Used mainly in high-silicon iron and to beneficiate ores.
[3] Mainly from 40 to 55 percent silicon.
[4] Used mainly in producing ferronickel.
[5] Used mainly in silicones and other chemical compounds.
[6] Includes calcium-silicon, calcium-manganese-silicon, silicon-manganese-zirconium, Ferrocarbo (including briquets), Alsifer, and other miscellaneous silicon alloys.

TABLE 6.—*U.S. imports for consumption of ferrosilicon and silicon metal, by grades and countries*

	1961			1962			1963		
	Short tons		Value	Short tons		Value	Short tons		Value
	Gross weight	Silicon content		Gross weight	Silicon content		Gross weight	Silicon content	
Ferrosilicon:									
8 percent and less than 60 percent silicon:									
Canada	13,094	2,179	$683,812	15,172	2,359	$782,588	12,781	1,962	$667,616
Germany, West	580	87	109,403	1,086	163	180,948	38	5	4,850
Total	13,674	2,266	793,215	16,258	2,522	963,536	12,819	1,967	672,466
60 percent and less than 80 percent silicon:									
Canada	35	24	6,438	53	37	9,366			
France				11	8	1,873	132	101	17,326
Italy							22	17	2,959
Norway				5	4	845	291	220	38,739
South Africa, Republic of	21	17	3,630	2	2	272			
Total	56	41	10,068	71	51	12,356	445	338	59,024
Grand total	13,730	2,307	803,283	16,329	2,573	975,892	13,264	2,305	731,490
Silicon metal:									
Canada				12	12	5,015			
France	31	30	8,206						
Total	31	30	8,206	12	12	5,015			

Source: Bureau of the Census.

TABLE 7.—*U.S. exports of ferrosilicon*

Year	Short tons	Value
1954–58 (average)	2,142	$410,082
1959	10,558	980,658
1960	5,501	867,140
1961	34,764	6,104,913
1962	4,101	1,348,661
1963	3,130	947,773

Source: Bureau of the Census.

PRICES

Prices of high-purity silicon are highly competitive and are generally quoted to customer's exact specifications as to doping, resistivity, and dimensions. Producers supply polycrystalline silicon in rods or pieces with or without dopants. Examples of 1964 nominal prices for 20 kilogram lots are as follows:

Polycrystalline up to 3 inches in diameter, n-type, 100 ohm-centimers without dopant.. $123.00/kg
Polycrystalline up to 3 inches in diameter, n-type, 200 ohm-centimers with dopant..... $139.00/kg
Float zoned refined single crystal in diameters of 30–33 mm, n-type..... $1.20/g
Special high resistivity single crystal over 2,000 ohm-centimers:
p-type..... $2.20/g
n-type..... $6.50/g
Source: Dow Corning Corp., Hemlock, Mich.

Prices of metallurgical silicon metal and silicon alloys vary with the quantity ordered, size required, method of packing, f.o.b. shipping point or delivered, and whether purchased on a contract or on the spot basis. Some alloys such as ferrosilicon are sold on a per pound contained silicon basis, others such as silicomanganese are priced on an alloy unit basis. Table 8 lists products and prices for 15-ton carlot bulk shipments.

TABLE 8.—*Prices of silicon metal, ferrosilicon and silicon alloys, October 1964* [1]

Type and grade	Percent silicon	Cents per pound gross weight
Silicon metal (0.35 percent max. iron)	98.40	19.00
Silicon metal (1.00 percent max. iron)	98.00	17.00
Silicon metal (0.3 percent max. calcium)	97.50	16.75
Silicon metal (low aluminum)	98.50	21.50
Ferrosilicon	50	[2] 13.60
Ferrosilicon (low aluminum)	75	[2] 16.50
Silicomanganese (1.50 percent max. carbon)	18–20	8.30
Ferrochrome-silicon (39–41 percent chromium)	42–45	11.40
Zirconium alloy (12–15 percent zirconium)	39–43	10.50

[1] Price based on 30,000-pound, bulk shipment.
[2] Per pound contained silicon.

RESEARCH

The Department of Defense sponsors applied research on high-purity silicon and other semiconductor materials. Research in the field of solid state microelectronics technology and other related research is conducted by the Air Force Avionics Laboratory, Wright Patterson AFB, Dayton, Ohio, and Electronics Research Directorate of the Air Force Cambridge Research Center, Bedford, Mass.

While the various services of the Department of Defense contribute considerably to the expanding technology, private industry has a large and very extensive research and development program. Most device manufacturers, as a result of research, introduced integrated circuitry (miniaturization) during 1964. An indication of the magnitude of current research was the introduction at a trade show of 125 new semiconductor products by one manufacturer.

OUTLOOK

The outlook is good for continued increase in the number of silicon electronic devices used. However, due to the trend to miniaturization, it is possible that the total quantity of high-quality silicon produced and used to make these electronic devices will not rise markedly. Continued growth should be experienced in the demand for silicones and other organo-silicons, with continued increase in new applications.

Consumption of ferrosilicon and other silicon alloys will grow with the demand for steel, and consumption of silicon metal should grow with the demand for aluminum.

The Nation's supply of raw material for the silicon industry is unlimited.

PROBLEMS

The problems of the high-purity silicon producer are serious ones. Profitability is dependent on large volume, and the producer is continually faced with the threat that his process or product will be quickly outdated as the result of a new development in technology—either the technology of silicon or that of a competing material. The rapidity, frequency, and magnitude of these changes can have serious adverse economic effects for a producing company. Further, the advances in utilization of the product are pointed toward miniaturization, so that quantity drops with improvement. Competition among the producers of high-purity silicon, foreign competition, and the competition from other materials are advantageous to the user but intensify the problems of the producer.

The problems of the silicon ferroalloy and metallurgical silicon metal producer are essentially the same as those of the other ferroalloy producers and are set forth in that chapter.

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SILVER

By J. Patrick Ryan [1]

SILVER has been mined through the ages in many parts of the world. Total world production of silver from 1493 to 1963 is estimated at 22 billion troy ounces, of which the United States contributed about 21 percent. Maximum annual production of the United States was nearly 75 million ounces in 1915. Mexico has been the leading silver-producing country since 1900; the United States ranks second. World output of silver for 1963 was estimated at 250 million ounces, of which the United States supplied about 35 million ounces, or about 15 percent. A substantial quantity of silver also is recovered from secondary sources in the United States.

For many years domestic output of primary silver has been obtained chiefly as a byproduct of base-metal and gold mining, and production has been determined chiefly by the output of base metals and gold.

Domestic consumption of silver in the arts and industry, and for coinage greatly exceeds domestic production. Most of the shortfall in industrial supply has been balanced by imports; coinage requirements have been furnished from the Treasury stock of nonmonetary silver. Similarly, in recent years world consumption of silver has exceeded world production by substantial amounts.

Most of the world's silver production in recent years has been used in various industries and the arts, but substantial quantities also are used in coinage in several countries. The principal nonmonetary uses are in the photographic and electrical industries, in manufacturing silver solders and brazing alloys, for sterling and plated silverware, and for jewelry and novelties. Large quantities of silver are also used in coinage and as monetary reserves.

The New York price of silver reached the monetary value of $1.293 per ounce in June 1963 after a more or less steady advance since November 1961 when Treasury sales at the fixed price of $0.91 per ounce were discontinued. The monetary price, at which silver is available for commercial use, provides an effective ceiling as long as Treasury policy regarding the conversion of silver certificates remains unchanged.

The expansion of domestic industrial and coinage requirements for silver in the past few years has increased the deficit in supply and brought heavy drafts on U.S. Treasury stocks. These stocks had been reduced at the end of 1964 to a point where continued withdrawal at the 1964 rate would result in exhaustion in 3 or 4 years; the drain during the last quarter of 1964 would cause depletion in 2 years.

Solution of the silver problem involves ways and means of increasing supply by increasing mine production and secondary recovery or reducing demand whether for the arts, industries, or coinage.

Resource development and research programs to develop new sources and more efficient use of silver are essentially long-range and results cannot be expected in the near future. Furthermore, production of silver is not normally responsive to increases in the price of silver because of the byproduct nature of most of the silver output and to limitations posed by the geological occurrence of silver deposits.

After long study and debate the Congress passed the Coinage Act of 1965, signed by the President on July 28, 1965, which authorized for silver-free 10-cent and 25-cent coins, 50-cent coins of 40 percent silver content and certain other silver economizing provisions. Development of substitutes for industrial use does not appear promising for reducing consumption.

Measured and indicated reserves of domestic silver-bearing base-metal ores are equivalent to a 17-year supply at the current production rate, and no doubt new ore will be developed as presently known ore is mined. However, the indicated productive rate, based on projections of base-metal output, is inadequate to supply projected domestic needs.

[1] Commodity specialist.

BACKGROUND

Silver, one of the earliest known metals, was first used by primitive man by shaping into ornaments. Evidence of the use of silver as early as the period 3000–2500 B.C. was disclosed by the discovery in Asia Minor of silver ornaments and utensils. This early silver probably was found as native metal, or as silver chloride which could be converted easily into bullion in a charcoal fire.

Silver was adopted by the Romans as the basis of their monetary system. The silver of Laurium, Greece, the most famous of the ancient silver districts, provided much of the wealth that won for Athens leadership among the Greek city-states. The mines at Laurium were worked for several centuries in the first millennium B.C. and had a total output of more than 250 million ounces. After discovery of America, most of the world's silver came from deposits in the Western Hemisphere. Bolivia, with a total production of more than 1 billion ounces, was the leading silver-producing country to 1700; the United States was the largest producer, except for a few years, from 1871 to 1900; Mexico has been the leading producer during most years since then.

The first monetary standard established in America was based on the value of silver. The first financial law passed by the Continental Congress in 1776 made the silver dollar the unit of value. The dollar was defined by Congress in 1792 as 371.25 grains of fine silver (412.5 grains of silver 0.900 fine). Except for minor variation with respect to alloy, that definition has not been changed.

Until the discovery of the Comstock Lode in Nevada in 1859, U.S. production of silver was insignificant (*4*).[2] Development of this great deposit and many others in the Western States placed the United States first in silver production for many years.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

In 1963, domestic mine production of silver was 35.2 million ounces of which one-third was recovered from precious metal ores and two-thirds as a byproduct of base-metal ores (fig. 2). Of the 25 leading domestic silver-producing mines, only four were worked principally for the silver value of the ore, 9 were copper mines, and the remainder were lead, lead-zinc or copper-zinc mines. The 25 mines supplied about 84 percent of the domestic output valued at $45.1 million. About 1,500 men were employed in mining and milling ores in which silver is the predominant metal recovered.

In 1963, the largest domestic silver mine was the Sunshine mine in the Coeur d'Alene region of Idaho. About 133,000 tons of ore was treated and 5.0 million ounces of silver was produced as well as substantial quantities of base metals as coproducts and byproducts. About 500 men were employed.

Silver has been found in most countries of the world and has been mined in recent years in more than 60 countries in all continents. In the United States, silver has been mined in 27 States. The principal silver-producing States in order of total output are: Montana, Utah, Colorado, Idaho, and Nevada; these five States contributed about 84 percent of the total domestic production. In order of recent output (1963) the five leading States are Idaho, Arizona, Utah, Montana, and Colorado.

Mexico has been the leading silver-producing country for many years, followed by the United States and Canada. The value of world production of silver in 1963 was about $250 million. The geographical distribution was as follows:

Country	*Production, million ounces*	*Percent of total*
Mexico	42.8	17
Peru	36.4	15
United States	35.0	14
Canada	30.7	12
U.S.S.R. (estimate)	27.0	11
Australia	18.9	7
Other	58.7	24
Total	249.5	100

About 99 percent of the domestic silver production in 1963 was recovered in the smelting of ores and concentrates; the remainder was recovered by amalgamation, cyanidation, and placer mining. In the United States, smelting and refining plants recovering silver and associated base metals are situated in several parts of the country near mines, centers of trade and commerce, and sources of low-cost fuel.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

The classification of silver ores is based on smelter terminology, smelter settlement contracts, and metal recovery originally adopted in 1905, except for modification necessitated by improvements in metallurgy and lowering of the grade of complex ore treated.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

The proportion of silver in bullion, coin or jewelry is usually expressed by its *fineness*, or parts a thousand. Fine silver is pure silver, 1000 parts fine or 100 percent silver. Sterling silver is 925 fine or 925 parts (92.5 percent) silver and 75 parts (7.5 percent) copper. Coin silver is 900 fine silver and the balance copper; and commercial silver bullion is 999 fine or higher. The troy system of weights is used in measuring silver as well as other precious metals and is based on the troy ounce of 480 grains or 20 pennyweight. There are 14.583 troy ounces in an avoirdupois pound.

TECHNOLOGY

Geology

Silver is commonly associated with base metals, chiefly lead, copper, and zinc, and most gold deposits contain silver. In deposits of these metals silver commonly occurs as a minor constituent of byproduct importance. Silver ores have been deposited in rocks of several geological ages, notably Tertiary, Cretaceous, and pre-Cambrian. Most of the world's silver has been mined from fissure veins or closely related deposits. The principal silver minerals of economic importance are argentite (Ag_2S), polybasite (Ag_9SbS_3), proustite (AG_3AsS_3), stephanite (AG_5S_4Sb), pyrargyrite (AG_3SbS_3), cerargyrite (AgCl), and native silver.

The Comstock Lode at Virginia City, Nev., from which silver valued at $225 million was produced from 1859 to 1911 is a fault fissure in tertiary andesite 2½ miles long and in places several hundred feet wide. The ore consists of argentite, polybasite and gold associated with pyrite and other sulfide minerals in quartz and calcite. Most of the minable ore was less than 2,000 feet in depth.

In the Cobalt district of Canada native silver deposits occur in narrow fissure veins in pre-Cambrian rocks associated with cobalt sulfides and arsenides. The veins are relatively small; however the deposits yielded around 375 million ounces in three decades following discovery in the early 1900's.

The silver ores of the Silver Belt in the Coeur d'Alene mining district of Idaho, which currently is the major silver-producing area of the United States, occur in veins in fault fissures and shear zones in pre-Cambrian quartzites and argillites in proximity to intrusive monzonite. The chief ore mineral is argentiferous tetrahedrite associated with sulfides of lead, copper, iron, and zinc in a gangue of quartz and siderite. Vein widths range from a few inches to 8 feet with mineralized zones as much as 30 feet wide. There are all gradations to the metal content of deposits in which the chief values are in silver.

Although the silver content of base metal ores may be extremely low, it can be recovered relatively economically by currently used refining methods. The porphyry copper deposits have a very low content of silver (0.02 to 0.11 ounce recovered per ton of ore), yet so great a tonnage of ore is mined and processed annually from these deposits that they are a major source of silver. In other ores silver is an especially valuable byproduct and may determine whether certain deposits can be worked profitably.

Mining

Methods of mining silver ore are similar to those used in mining several other metal ores and vary considerably from one mine to another, depending on such factors as size and shape of the ore bodies, physical and mineralogical character of the ore and surrounding rock, and depth of mining.

The Sunshine mine, the largest domestic silver mine, is serviced essentially by one main shaft 4,000 feet deep and five winzes. A sixth winze, the No. 10, has been completed to 125 feet below the 4,600 foot level. Development drifts are driven on the veins at level intervals of 150 and 200 feet and raises are driven between levels at approximately 100-foot intervals depending upon the characteristics of the ore. Stope blocks thus are about 100 feet long. The ore is mined by a hydraulic cut and fill method utilizing sand fill, an occasional rock bolt, but little timber. Ore is broken by breasting down using jackleg drills with carbide tipped rods and ammonium nitrate-fuel oil explosive. Broken ore in stopes is scraped to a chute in the timbered raise, loaded from the chute into 40-cubic foot cars, and transported by battery locomotives to the shaft pockets and hoisted to surface. In 1963 the ore averaged 38 ounces of silver a ton, 0.58 percent lead, and 0.71 percent copper.

Metallurgy

The argentiferous ores of the ancient mines at Laurium were treated by washing on stone tables and smelting the resulting concentrate, or by direct smelting, depending on the quality of the ore. The silver-bearing lead bullion produced by smelting was refined by cupellation to recover the silver. The amalgamation process by which metallic silver is wetted and becomes alloyed with mercury was first used in 1540. About 1850, the Augustin process was developed, in which the ore was roasted with common salt to convert the silver minerals to chlorides, followed by leaching with hot brine

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and precipitation with metallic copper to recover the silver.

The Patio process which came into use in 1557 for the treatment of silver ores at Pachuca, Mexico, utilized a chloridizing roast, brine leaching, and amalgamation. The Washoe process, or pan amalgamation, was developed at the Comstock mines, Washoe County, Nev. In this process the crushed silver ore was ground in large cast-iron pans, mercury and salt were added to the steam-heated pulp, and the silver subsequently was recovered from the resulting amalgam by retorting. The Patera process which followed the Augustin and Patio processes was first applied to the ores of the Joachimsthal district, Bohemia. This process utilizes the solubility of silver chloride in a solution of sodium hyposulfite, and subsequent precipitation of the silver as silver sulfide (Ag_2S) by sodium sulfide (Na_2S).

Chlorination and hyposulfite leaching were superseded by cyanidation by 1900 and later by flotation combined with smelting. Cyanidation of silver ores, however, is still practiced in some districts in Mexico and Central America.

Byproduct silver from base-metal mines follows the ores produced through all stages of mining, direct shipping or concentration and shipping, smelting, and is ultimately recovered in the precious metal units of base-metal refineries. Losses of silver in the concentration processes are about the same as those for base metals. Average unit recoveries of silver in ounces per ton from base-metal ores of various classes in the United States in 1963 were copper ore, 0.08; lead ore, 1.09; zinc ore, 1.01; other base-metal ores, 1.41.

Silver ore from the Sunshine mine is crushed in gyratory and cone crushers and ground in ball mills in closed circuit with Akins classifiers to 60 percent through 200 mesh. The ore pulp is treated in Fagergren flotation cells, and a bulk concentrate containing 90 to 95 percent of the silver-bearing tetrahedrite and 75 percent of the silver-bearing galena is recovered. A tetrahedrite concentrate is floated in a retreatment circuit and sent to the antimony plant where antimony and arsenic are removed by caustic Na_2S leach; the high-grade silver-copper residue is washed and filtered and shipped to a copper smelter for recovery of silver and copper. The galena depressed in the retreatment flotation circuit is collected in settling cones filtered and shipped to a lead smelter for recovery of silver and lead. Mill recovery is about 97 percent of the silver and copper and 93 percent of the lead.

Silver in lead ores is carried down with the lead in smelting and is recovered by the Parkes process. This process consists of stirring zinc into the molten lead bath heated to above the melting point of zinc and allowing the mixture to cool slowly. A zinc crust containing the silver separates and can be skimmed from the lead, the zinc is driven off by distillation, and the residue is cupelled to dore silver. The silver in copper ore follows the copper in smelting processes, and in the electrolytic refining of copper, the silver remains in the anode slime from which it is recovered as silver bullion by smelting. The silver produced with gold in gold-placer mining or lode gold mining is recovered in the electrolytic refining of gold bullion.

Crude silver bullion, contains gold and sometimes small quantities of other metals, and is refined by electrolysis, using an electrolyte of silver nitrate and nitric acid. The refined silver is cast into ingots that have a purity of over 99.9 percent.

USES

Although silver has been used for centuries for coinage and the arts, it also has many essential uses in industry. Silver bullion also serves as backing for paper currency.

Some of the properties that make silver valuable in the arts and industries are attractive color and ability to take a fine finish; high malleability and ductility; high electrical and heat conductivity; resistance to corrosion and the sensitivity to light of some silver salts.

The principal industrial uses of silver are in the manufacture of photographic materials, in the fabrication of sterling silverware and electroplate and in silver solders and brazing alloys. Large quantities of silver are used for jewelry, optical goods, and novelties. Silver is also used in the manufacture of various chemical products for the laboratory, and for caustic, astringent and antiseptic purposes in medicine. Dental amalgams and alloys also consume important quantities of silver. Silver solders and brazing alloys made by alloying silver with varying proportions of base metals such as copper, zinc, and cadmium are widely used in the electric-appliance, air-conditioning, and automotive fields for joining pipes, making electrical connections, and forming mechanical assemblies. These alloys are being employed to an increasing extent for high-temperature applications in jet aircraft and in cooling rocket nozzles.

Substantial quantities of silver are used for electrical contacts in such regulating equipment as light-duty relays in telephone and aviation equipment, fluorescent-lamp controls, electromagnetic counters, and in protective devices for motors, and thermostats. Other growing industrial uses for silver include decorative finishes on ceramic materials, high-efficiency silver-

zinc and silver-cadmium batteries in jet aircraft and guided missiles, portable television cameras and scientific instruments that require high power output with minimum size and weight.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Gold is usually associated with silver in nature and is recovered as a byproduct or coproduct of some silver ores. Lead is commonly recovered as a byproduct or coproduct of silver-lead ores, and copper, zinc, antimony, bismuth, and arsenic are also byproducts in some silver ores. Tin is a coproduct of silver in some ores in Bolivia, and cobalt, uranium, and radium are coproducts of silver in some ores in Canada and Africa.

ALTERNATE MATERIALS

Silver in coatings on light-sensitive photographic paper for office copy work has been largely replaced by Xerography, an electrostatic duplicating process. Stainless steel is an alternate material for silver flatware, particularly in commercial use, and constitutes a large part of the market for tableware.

Aluminum and rhodium are substituted for silver for reflectors and amalgam in dental fillings; and tantalum can be used in place of silver for plates, sutures, and pins in surgery. The total substitution of other materials for silver is small, however, in comparison to the total consumption.

Cupro-nickel, nickel and other base metals have replaced or are replacing silver coins in some countries including the United States where subsidiary silver coinage is to be replaced by copper coins clad with cupro-nickel or 80-percent silver alloy as provided in the Coinage Act of 1965.

SECONDARY SOURCES AND RECOVERY

A constant flow of new scrap generated in manufacturing processes but not consumed in end products is returned to refiners for reuse. This material includes waste from metal stampings and coin manufacturing, turnings and anode butts. Silver is also recovered from used products such as batteries, mirrors, photographic film and plates, silverware, alloys, jewelry, and silver-plating and photographic solutions. According to the Bureau of the Mint, in the United States an average of approximately 60 million ounces of silver was returned from industrial use annually during the period 1959–63.

RESERVES

United States

Most of the United States reserve is in the Western States, but small amounts of silver are recovered as a byproduct of other metals in the Central and Eastern States. Measured and indicated reserves of silver, minable at or near current metal prices, total 590 million ounces (table 1), equivalent to a 17-year supply at the 1963 rate of production. About 90 percent of the reserve is contained in base metal deposits, compared with only 9 percent in deposits mined chiefly for silver. The exploration and development of inferred reserves will augment measured and indicated reserves and extend the productive life of currently operating mines. In addition new discoveries are almost certain to be made which will further augment known reserves. However, as most of the reserves are in base metal deposits, output of silver will be closely related to base metal production. Thus, domestic reserves of silver in silver-bearing deposits are adequate to supply silver for several years at, or moderately above, the current annual rate of output, but, because of limitations on annual output, the reserves are not adequate in terms of supplying silver at a high enough rate to meet domestic demand.

TABLE 1.—*Silver reserves of the United States, classified by type of ore*

Type of ore	In measured and indicated ore		In inferred ore	
	Million troy ounces	Percent of total	Million troy ounces	Percent of total
Straight silver	52.7	9.0	85.0	10.0
Lead-zinc-copper	236.0	40.0	570.0	67.0
Copper-zinc	.4		8.2	1.0
Copper	295.0	50.0	170.0	20.0
Gold	5.3	1.0	4.0	2.0
Tungsten or iron	.7		.6	
Total (rounded)	590.0	100.0	840.0	100.0

Foreign

Reliable data on reserves of silver in most foreign countries are scarce or entirely lacking. Estimates of reserves of the principal silver-producing countries of the free world shown in table 2 are based on reserves of silver-bearing base metal ores and the average ratio of the output of silver to the output of base metals. Like domestic reserves, the free world silver reserve, totaling 2.7 billion ounces, is adequate to supply silver for many years at, or moderately above, the annual rate, but because most of the output of silver is limited by the output

of associated base metals, the reserve is not adequate in terms of supplying silver to meet demand at the current level.

Discoveries of silver-bearing ore in the past few years, now being explored and developed in several countries, especially in Canada, Australia, and the United States, have not been fully evaluated but will add substantially to the total world reserve in the foreseeable future. Furthermore, intensive exploration prompted by substantial increases in the price of silver and associated metals, lead, zinc, and copper, is expected to result in new ore discoveries and ultimately increased production of silver.

TABLE 2.—*Estimated silver reserves and production of the principal free world countries*

Country	Production in 1963 (million troy ounces)	Reserves (measured and indicated) (million troy ounces)	Years supply at 1963 output rate
Canada	30.7	640	21
United States	35.2	590	17
Mexico	42.8	734	17
Peru	36.4	528	14
Australia	18.9	259	14
Total	164.0	2,751	17

Monetary stocks of silver in the U.S. Treasury at the end of 1963, comprising bullion and coin, totaled 1,584.3 million ounces. Silver held outside the Treasury in coins aggregated 1,716.3 million ounces.

Substantial quantities of silver as coinage in circulation are held in several countries, but data on world monetary stocks are incomplete.

SOURCES OF STATISTICAL INFORMATION

Statistics on mine production of silver in the United States are gathered, analyzed and compiled by the Federal Bureau of Mines in cooperation with the Geological Surveys of some States. The data compiled permit monthly and annual reports on mine production including information on sources and types of ore, methods of treatment, and recoveries.

Data on refinery production and on domestic and foreign consumption of silver are compiled by the Bureau of the Mint (*2*) and data on foreign trade in silver are supplied by the Department of Commerce. Monthly bulletins of the U.S. Treasury Department publish detailed data on monetary silver stocks, and silver in circulation as coinage. Daily statements show changes in the Treasury stocks and the relation of monetary reserves to nonmonetary reserves. Transaction Statements of the Bureau of the Mint also give detailed information on stocks, acquisitions, sales, and withdrawals for coinage and commercial use.

Silver production statistics are published by some foreign countries, especially those of the British Commonwealth, but corresponding data from other countries are not complete. The Bureau of Mines publishes a report on world production of silver based on information obtained from questionnaires sent to each country, consular reports, official publications, and company reports. Reliable data from Soviet-bloc countries are significantly lacking.

PRODUCTION, CONSUMPTION, AND TRADE

Since World War II, world output of silver has increased steadily reaching an average of about 234 million ounces annually for the period 1954–63. Domestic production has been moderately stable in the post-war period, averaging about 36 million ounces annually since 1950. Thus, in recent years U.S. mines produced about 15 percent of the total world silver output.

It has been estimated that about one-third of the total world output of silver is in circulation as coinage or held by governments for monetary purposes; one-third is privately owned; and one-third has been lost or dissipated.

World production of silver from the discovery of America to 1963 was approximately 22 billion troy ounces or nearly 763,000 tons. About four-fifths of this total was produced in the Western Hemisphere with North America contributing about 60 percent and South America 20. Mexico produced about 35 percent of the world total, the United States 21, Peru 9, and Bolivia 9.

World production of silver reached a peak of 278 million ounces (9,530 tons) in 1937; U.S. maximum annual production was nearly 75 million ounces (2,570 tons) in 1915. In 1963 world output of silver was estimated at 250 million ounces, and output of United States was approximately 35 million ounces (fig. 1).

The domestic supply of silver for industrial needs is obtained normally from mine production, secondary returns, and imports.

U.S. consumption of silver in the arts and industries, and for coinage greatly exceeds production. In recent years free world consumption in the arts and industries for coinage also has exceeded total production. For the period 1959–63 estimated free world consumption of silver averaged nearly 302 million ounces annually, of which nearly 60 percent was consumed by the United States. Summarized data on silver consumption in the arts and industries of the United States are given in table 3. No

current breakdown by end uses is available, however, photographic supplies, sterling and plated silverware, electrical products, and brazing alloys constitute the principal use of silver in the arts and industries. In 1963 it was estimated that the manufacture of photographic materials accounted for about 30 percent of the total silver used; electrical and electronic equipment, 24 percent; silverware and jewelry, 20 percent; brazing alloys and solders, 12 percent; space and defense applications, about 9 percent; and the remainder in miscellaneous uses. Imports and mine production furnished about three-fourths of the total industrial and defense silver requirements; the remainder was supplied from Treasury stocks.

The quantity of silver used in minting subsidiary coins averaging slightly more than 50 million ounces in the preceding 5 years rose to 111.5 million ounces in 1963. U.S. coinage requirements normally constitute about one-half of total silver used in free world coinage; however, in 1963 U.S. coinage requirements constituted nearly two-thirds of total silver used in free world coinage. Rising domestic coinage requirements in recent years was attributed to the growth in the use of coin-operated vending and metering machines and withdrawals of coins from circulation by collectors and speculators.

In 1963 the United States imported silver ore, base bullion, refined bullion, and silver coins valued at $71 million from some 28 countries. In the same year it exported the same items valued at $42 million to 17 countries. Foreign trade of the United States in silver for the period 1954–63 is shown in table 4.

The United States imposes no duties on imports of silver in ores, bullion, or coins, but does levy duties on products ranging from 10–10.5 percent on silver compounds to 55 percent on semimanufactured silver.

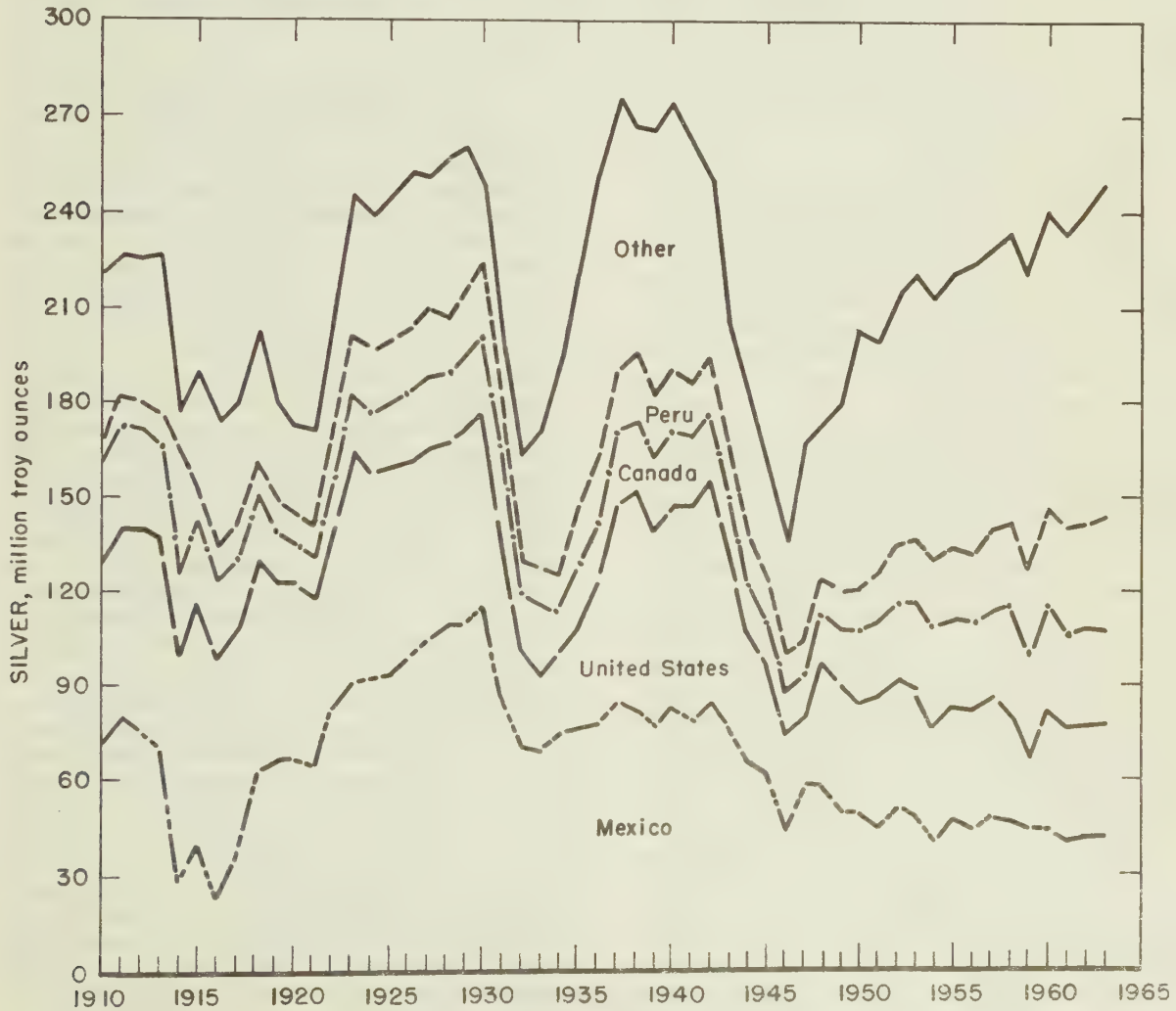

FIGURE 1.—World Production of Silver.

TABLE 3.—*Net industrial [1] consumption of silver in the United States*

[Million troy ounces]

Year	Issued for industrial use	Returned from industrial use [2]	Net industrial consumption
1954–58 (average)	122.7	29.0	93.7
1959	143.0	42.0	101.0
1960	151.0	49.0	102.0
1961	155.8	50.3	105.5
1962	180.8	70.4	110.4
1963	204.5	94.5	110.0

[1] Including the arts.
[2] Includes secondary materials to monetary use, jewelry, plate, scrap film, and other forms of scrap.

SOURCE: U.S. Bureau of the Mint.

TABLE 4.—*Value of silver imported into and exported from the United States*

[Millions]

Year	Imports	Exports
1954–58 (average)	$114.4	$7.0
1959	62.7	9.9
1960	57.4	25.8
1961	45.4	37.9
1962	74.5	15.1
1963	70.9	41.8

SOURCE: Bureau of the Census.

STRATEGIC CONSIDERATIONS

Most of the silver mined in the United States is a byproduct or coproduct of base-metal or gold ore. In some silver-bearing base-metal ores, the value of the recoverable silver may be an important factor in economic feasibility of mining and production of base metals needed for peacetime industrial uses and for vitally essential purposes in wartime.

Silver had incalculable value to the United States and its allies in World War I in obtaining supplies from far eastern countries where silver traditionally has been the principal monetary metal. A somewhat similar situation developed in World War II when large quantities of silver from Treasury stocks were loaned to our European allies. In addition a large quantity of silver was sold to industry by the Treasury for purposes approved by the War Production Board. During World War II, silver was first used for plating bearings of aircraft engines and for mechanized equipment where high-duty service and long life were essential. A large quantity of silver from Treasury stocks was loaned to the Defense Plant Corporation during World War II for use as electrical busbars, thus releasing copper for other needs. The total silver utilized in World War II exceeded 1,480 million ounces or about 40 times the total domestic production in 1963. U.S. Treasury stocks of silver bullion securing silver certificates are large, and large quantities of silver are in circulation as coinage. Total Treasury silver, both inside and outside the Treasury, represent a stockpile of over 3 billion ounces and, in an emergency, legislation could be enacted to release silver for military purposes from this vast stock.

Domestic consumption in recent years has been about three times production with the supply deficit being balanced by imports and withdrawals from the Treasury stock. Estimates and projections of silver supply and requirements indicate that consumption probably will continue to exceed available new supply by progressively increasing quantities in the short-term future. At the projected rate of withdrawal, the Treasury stock is not adequate to balance the deficit in supply for both industrial and coinage requirements after 1967 and the stock could be virtually depleted by 1968. The impending depletion of the Treasury stock would require that a strategic stockpile for silver be established to provide for emergency demand.

GOVERNMENT PROGRAMS

The Silver Purchase Act of 1934 and subsequent amendments of 1939 and 1946 significantly affected domestic price, production, and consumption of silver for many years. Large quantities of silver were purchased under the Government's buying program, and substantial sales were made to domestic consumers from Treasury free stocks until sales were discontinued late in 1961.

Consumption and use of silver in industry and the arts was controlled by War Production Board regulations during World War II. Treasury silver, in effect, was eligible for essential industrial and military uses; domestic silver was permitted in silverware, jewelry, watchcases, church articles, and other items classed as nonessential; and foreign silver was limited to use in photography, electrical appliances, dental and medical supplies and other items with preference ratings.

The Bank of Mexico acquires large quantities of silver from mining companies in Mexico, maintains substantial stocks to cover foreign commitments, and exercises some control on trading through the issuance of export licenses to producers.

The repeal in June 1963 of the Silver Purchase Act, and the tax on transfers of silver bullion, combined with redemption of silver certificates, largely freed silver from government control. However, the availability of silver from the Treasury continued to be the principal stabilizing factor in the world market.

Silver became eligible for government financial assistance under the program administered by the Office of Minerals Exploration in June 1961. The percentage of Government participation in the exploration of silver deposits was raised in October 1964 from 50 to 75 percent to provide greater incentive to search for and explore new silver deposits that might lead to increased production and help to alleviate the domestic supply shortage.

The Geological Survey initiated a reconnaissance program in 1964 designed to outline favorable areas for the occurrence of near-surface silver deposits. The work includes geological mapping and geochemical studies and utilizes as ore guides the distinctive hydrothermal alteration halos and geochemical anomalies associated with epithermal deposits. New tools and geophysical techniques applicable to silver exploration also are being tested.

PRICES

In 1933 the Treasury was authorized, under Presidential Proclamation 2067, and by Congress (31 U.S.C., secs. 316c and 316d), to acquire for coinage newly mined domestic silver with seigniorage deduction of 50 percent. Based on the monetary value of the silver dollar of $1.2929 per fine troy ounce, the Treasury buying price was thus fixed at $0.6464 per ounce. The monetary value of the silver dollar is based on the fine silver content of the standard silver (371.25 grains or 0.7734 fine ounces).

The Treasury price subsequently decreased to $0.5001 in August 1934; increased to $0.7757 in April 1935; decreased to $0.6464 in January 1938; and increased to $0.7111 in July 1939. The latest change in the Treasury price to $0.905+ per fine troy ounce, was effected by act of Congress (60 Stat. 750, 31 U.S.C., sec. 316d) on July 31, 1946, when the seigniorage deduction of 30 percent was set for services performed by the Treasury relative to the coinage and delivery of silver dollars.

Under authority of the act of July 31, 1946, Treasury silver became available to domestic consumers from its nonmonetary or free stocks at a selling price of $0.91 per fine ounce for delivery at the San Francisco Mint; and $0.91 plus the equivalent of railway express charges from San Francisco, or effectively $0.9225, at the New York Assay Office.

The New York price as quoted daily by Handy & Harman represents the actual price at which refined silver, in commercial bar form of acceptable brand and quality, was offered to Handy & Harman for New York delivery in quantities sufficient to meet daily requirements.

The buying and selling activities of the U.S. Treasury, which had been the chief factor stabilizing the price of silver in world markets for several years, became essentially inoperative following the Presidential order terminating Treasury sales in November 1961. Following cessation of Treasury sales the New York price began a general rise from the equivalent Treasury selling price of approximately 92 cents at New York to $1.293 an ounce, the monetary value of silver, in September 1963, after which it remained unchanged through 1964.

Repeal of the Silver Purchase Acts and the silver transactions tax in June 1963 permitted resumption of trading in silver futures on the New York Commodity Exchange for the first time since 1934. Prices for forward delivery exceeded the New York spot price by a considerable margin ranging up to 9 cents an ounce premium in September 1964 for delivery in August 1965. Amendment of the Federal Reserve Act permitting the replacement of $1 and $2 silver certificates by Federal Reserve notes effectively established a ceiling on the market price of silver at its monetary value of $1.293 per ounce since silver became available for commercial use through redemption of silver certificates.

Prior to cessation of Treasury sales and repeal of the Silver Purchase Laws, the average price of silver in the London market remained relatively stable, fluctuating in a narrow range near the fixed buying and selling prices of the U.S. Treasury. In 1963 spot prices in London did not vary much from the equivalent New York price, reflecting the cost at New York plus transportation to London and sterling-dollar exchange.

After long study in the executive departments and extended hearings before congressional committees, the Congress passed the Coinage Act of 1965 which the President signed on July 28. The Act provided for the elimination of silver from 10-cent and 25-cent coins substituting coins with a copper core clad with cupronickel alloy adn the reduction of silver in the 50-cent coin from 90 to 40 percent by the introduction of a copper core coin clad with an 80 percent silver alloy; other provisions give the President considerable authority in effecting a smooth transition to the new coinage system.

The average New York price for silver for the period 1910–63, and the U.S. Treasury price from 1933 to 1961 are shown in figure 2.

TAXES

Silver mining, refining, and manufacturing industries are taxed the same as other industries. The 10 percent excise tax levied on the

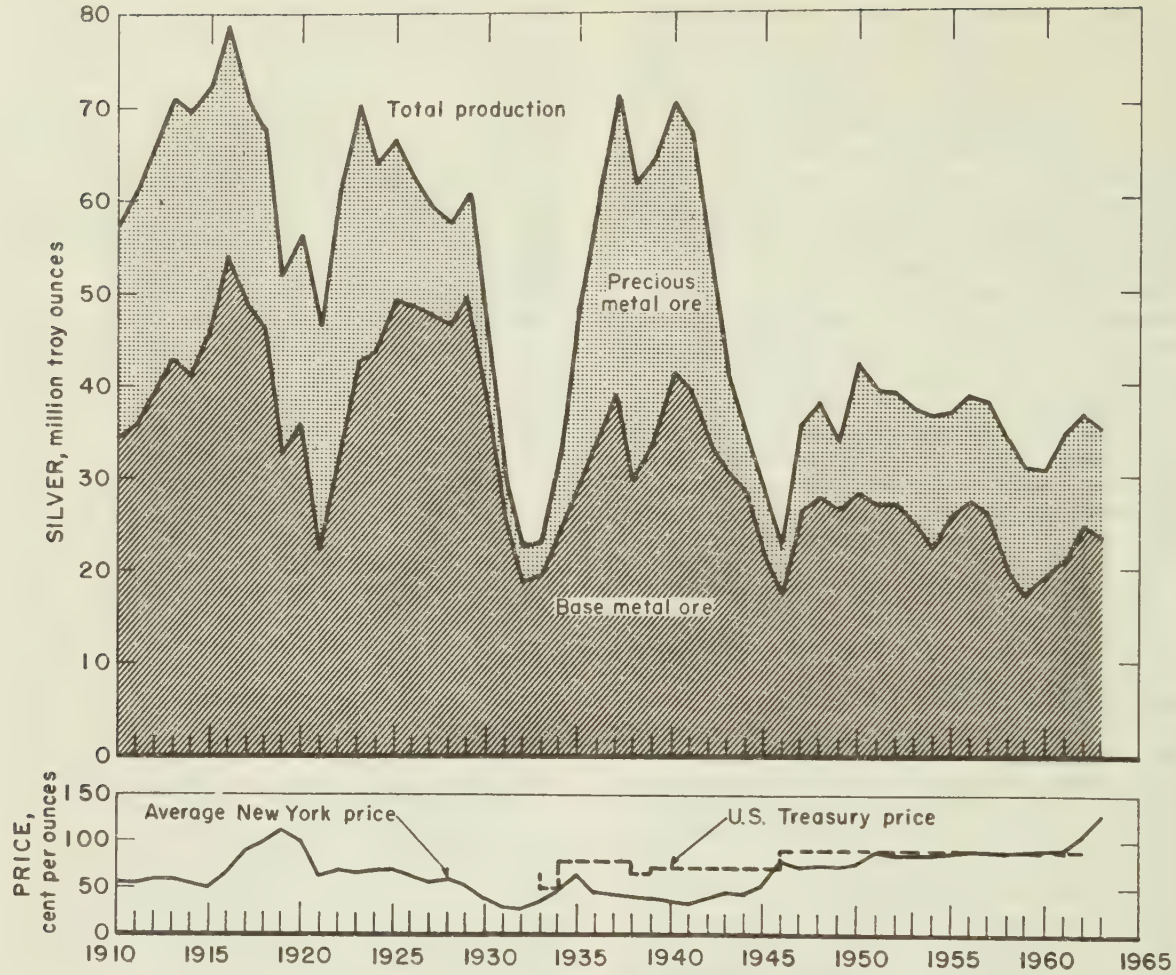

FIGURE 2.—Silver Production in the United States and Price Per Ounce.

sale of luxury items made of silver was repealed June 22, 1965.

The depletion allowance for silver is 15 percent of the gross income both domestic and foreign.

RESEARCH

Metallurgical research to adapt basic processes to the recovery of silver and other metals from refractory ores is conducted by various mining companies and ore-testing laboratories. Also, extensive research to develop new uses leading to increased consumption of silver was carried out in the 1930's by the American Silver Research Project, an organization of the principal silver producers and dealers. Areas of research investigation by this organization, included: Properties and technology of silver, binary and ternary alloys of silver, low and high-temperature bonding, silver in bearings, coatings, stationary and moving electrical contacts, corrosion resistance of silver and silver alloys, and silver as a catalyst and as a fungicide. The investigations pointed up areas where use of silver could be expanded, such as corrosion-resistant coatings on containers, catalysts in chemical process industries, and electrical contacts.

Bureau of Mines research in mining and metallurgy yields information contributing to greater efficiency and safety in mining, better evaluation of mineral resources, increased recovery of silver from ores and wastes, and more effective utilization of silver.

The Bureau recently began investigations to determine if recovery of silver from large low-grade deposits is economically feasible by the application of newer hydrometallurgical techniques of extraction. These studies include the use of ion-exchange resins and solvent-extraction tehniques to concentrate silver-bearing solutions, nitric acid leaching procedures, and a thorough evaluation of combined flotation-leaching-electrolytic recovery methods.

The Bureau also is surveying possible use of substitutes for silver in industrial applications such as transpiration-cooled rocket nozzles, high-temperature solders and brazing materials, and dental amalgams. Major industrial losses of silver are being studied by Bureau engineers to determine if current collection methods for scrap and waste silver-bearing materials can be improved and if current secondary silver reclamation technology is adequate.

Research on developing improved methods of sampling ores and evaluating mineral deposits and in applying new scientific techniques in mine planning and operation has yielded information useful to silver as well as other metal mining. Studies were begun by the Bureau in 1964 of low-grade deposits which could not be mined during earlier days, but which might be economically recoverable through the application of improved evaluation techniques and the use of modern low cost surface or underground mining methods. New mining techniques which provide for the prevention or control of rockbursts are currently being studied. This problem may become a serious handicap to production in deep mines.

OUTLOOK

The outlook for consumption of silver in the United States and in the world was profoundly affected by the signing of the Coinage Act of 1965 on July 28. The replacement of most of the silver in United States subsidiary coinage with base metals should go far toward righting the serious imbalance in silver supply and demand that has been growing in recent years. The output of silver from mines in which silver constitutes more than 50 percent of the value of the ore probably will continue to yield about one-third of the domestic production. The recovery of silver from secondary sources is expected to increase slightly in the next 4 or 5 years as primary consumption grows. Net imports probably will constitute a much smaller part of domestic supply in the next few years than in past years, as surplus stocks in foreign countries appear to be largely depleted.

Net industrial consumption is expected to increase about 1.5 to 2.0 percent annually in the foreseeable future. The use of silver probably will continue to grow in industrial or defense-oriented products, while its use in other consumer materials may level off or decline. The sharp rise in the quantity of silver used in coinage since 1961 may continue in the next few years, assuming no change in the present coinage policy.

As long as the Treasury continues to redeem silver certificates at the monetary price of $1.293 an ounce, this price establishes an effective ceiling on the New York market price.

As most of the world production of silver is recovered as a byproduct or coproduct of copper, lead, and zinc ores, any substantial increase in new supply will be dependent largely on the output of associated base metals. Hence, prices and other factors affecting production of base metals will, to a large extent, continue to determine the output of silver.

In recent years, intensive exploration using new and improved scientific techniques has resulted in the discovery of substantial deposits of silver-bearing ores in various countries of the free world.

Current and planned development of the new silver-bearing ores, and expansion of production facilities at established mines particularly in Canada, Peru, and Mexico, and to some extent in the United States, will eventually lead to greater silver output and thereby aid in reducing the overall supply deficit. Unless some unforeseen industrial or defense applications requiring substantial quantities of silver are developed, free world mine production may ultimately approach a balance with industrial consumption.

Silver will continue to find new uses in industry where its superior electrical and thermal conductivity, excellent reflectivity, malleability and ductility, and good corrosion resistance justify its high cost.

The rapid expansion of the electronics industry has created increased demand for silver contacts, conductors, and other silver-bearing components in fabricating various electrical and electronic equipment.

New applications of silver in military and consumer products continue to be developed. The use of silver-zinc and silver-cadmium batteries continues to increase in response to demand for a compact, dependable power source of high capacity not only for space and military equipment, but for industrial and consumer applications as well. High-energy silver chloride-magnesium batteries were developed to power torpedoes, sonar equipment and other equipment used in submarine warfare. The use of high-silver alloys in brazed honeycomb assemblies capable of withstanding high-temperature service conditions may be expected to

increase as the production of advanced aircraft and space vehicles expands. In addition to rocket motor applications, silver-infiltrated tungsten is being used as electrical contacts and for rotating bearings. The use of silver alloy contacts in electrical relays to control circuits in computers and tabulators continues to expand as demand for these machines grows. The recent development of photochromic glass containing silver halide for protection from solar light and heat has large potential use and may ultimately require a substantial quantity of silver.

The continued growth in the quantity of photographic materials used in amateur, professional and commercial photography will probably offset any reduction in the silver content of such materials and photographic materials likely will continue to be the leading silver-consuming industry.

The expanding use of coin-operated, merchandise-vending machines and meters will probably continue to absorb increased quantities of silver coins. The withdrawal of large quantities of silver coins from circulation by collectors and speculators is likely to continue at least in the near future.

PROBLEMS

Consumption of silver in the arts and industries and for coinage has exceeded new production since the early part of World War II, and the supply deficit has accelerated since 1958 as increased demand continues to outrun new production. The status of silver in the world economy has thus reversed from one of overproduction and correspondingly low world market prices, prior to World War II, to one of underproduction, in spite of price increases in postwar years. Thus, the paramount long-term silver problem is to find and develop new supply sources that can meet growing demand before world stocks are depleted.

Silver mining has many economic and technologic problems common to other deep level underground mining operations. Basically they are cost problems connected with breaking rock underground, ground control, ventilation, and transporting ore to central hoisting stations, and to concentrating and smelting plants to recover the relatively small quantities of silver and other metals it contains.

Many of the fundamental physical factors relating to the environment and extraction of ore from mineral deposits are not well understood and, although advances in mining technology have been notable in recent years, much of the technique of mining continues to be based on empirical methods rather than scientific principles. This deficiency in fundamental knowledge of the physical and mechanical properties of rock associated with mineral deposits has been a contributing factor in preventing maximum efficiency in mineral extraction and reduction of the cost of mining. Solution of problems restricting mineral extraction would result ultimately in greater production of silver and associated metals at some mines. Although offset to some extent since 1960 by higher world market prices, operating costs have continued to increase and some mines, where silver is the principal metal recovered in terms of value, have been forced to mine higher grade ore and abandon reserves that have become submarginal.

Problems relating to the exploration of small and widely distributed silver-bearing ores are chiefly economic. The high capital costs of mining and milling facilities in some remote areas and the relatively high operating costs of small-scale operations are deterrents to the development of new mines. Production capacity at most silver mines is limited or determined largely by the shape, size, and depth of the orebodies. Most of the deposits at silver mines are narrow veins or replacement masses lying deep in the ground. The orebodies are commonly irregular, discontinuous, and enclosed by fractured and altered wall rocks, making it difficult and expensive to extend and support mine openings. These physical conditions and high cost of exploration and development are factors restricting the scale of mining and fixing the capacity of reduction facilities. Hence, production capacity is relatively inflexible and not readily responsive to increases in demand for silver.

Serious deficiencies exist in consumption statistics on silver, needed by producing and consuming industries and government agencies, because of incomplete data on quantities used in various industries. This lack of reliable data on the end use pattern is a serious handicap in assessing trends and estimating future demand and in connection with developing a comprehensive program for silver.

Up-to-date information is lacking on the economic relationship of the production of silver to that of associated base metals and on the extent that price changes of associated base metals af-

fect silver output, and conversely, the effect of price changes of silver on the output of associated base metals.

Basic data on the preparation and properties of some silver alloys, such as silver-palladium, are needed to fully assess their current and potential use. Better knowledge of properties would aid in developing new and improved products and more efficient utilization of silver in industrial processes.

Substantial quantities of silver are consumed in fabricating silver infiltrated tungsten nozzles for rocket motors. The silver used in silver infiltrated tungsten is vaporized at the very high temperatures created by solid rocket fuels and is nonrecoverable.

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SODIUM

By William H. Kerns [1]

SODIUM and chlorine, supplied primarily by salt, are as essential to man as air, water, and food. Sodium compounds play a part directly or indirectly in the preparation, processing, or production of virtually everything he eats, drinks, touches, and sees.

The commodities covered in this chapter are sodium chloride, sodium carbonate, sodium sulfate, and metallic sodium. Sodium chloride, common salt, is a plentiful mineral commodity. Exclusive of the oceans and salt lakes, which contain inconceivably large quantities of dissolved salt, vast amounts are found in underground deposits scattered throughout the world. The United States has virtually an inexhaustible reserve of salt despite an annual consumption exceeding 31 million tons.

More than one-half of the salt output each year is produced as salt brine from underground deposits and used as such, more than one-quarter as rock salt by underground mining, and the remainder as evaporated salt by solar, vacuum pan or open pan evaporation of natural or artificial brines. Salt is produced by 57 companies at 95 plants located in 17 States. Imports account for 4 percent of the U.S. apparent consumption and exports are about one-half of the imports. The annual salt production rate of increase has correlated closely with the growth rate of gross national product (GNP). Using this as a base, production should double by 1980 and quadruple by the year 2000.

The largest consumer of salt is the chemical industry, which uses two-thirds of the annual output. The production of chlorine-caustic alone consumes one-third of the total domestic salt output, while that of soda ash consumed one-fifth of the total. The trend of an increasing proportion of the salt output being used each year for chlorine production accompanied by a decreasing amount consumed in manufacturing soda ash is expected to continue. Quantities of salt used for road stabilization, highway snow and ice removal, and for regeneration of water softeners using the ion-exchange principle are expected to increase each year.

Problems of the salt industry are chiefly those of maintaining the same or lowering production and marketing costs so that salt may continue as a high-volume low-unit-cost commodity. Quoted prices for salt have remained steady since 1958, average reported selling price or value at place of production has decreased slightly, and packaged-salt prices have remained virtually stable. As an example, a 26-ounce box of salt costing 10 cents in 1925 costs 11 cents today. Prices are maintained through constant improvements in mining, producing, processing, handling, and marketing methods. Other problems relate to the corrosive nature of salt solution on plant equipment and on vehicles and roads when salt is used for snow and ice removal.

Sodium carbonate (soda ash) requirements of nearly 6 million tons per year are supplied by manufactured soda ash from 11 ammonia-soda (Solvay) process plants in the East and Midwest and from natural sources of trona mined at 2 operations in Wyoming and from brines at 3 operations in California; 81 percent of the total is manufactured and 19 percent is natural. The growth in the soda ash industry is expected to continue to be largely from natural soda ash rather than ammonia soda production because new ammonia soda plants are too expensive compared with natural soda ash production installations. This has resulted in new and expanded natural soda operations and exploration and development work on other prospective operations. U.S. soda ash imports for consumption are negligible, but exports are 3 percent of the U.S. production and have increased each year for the last decade.

Reserves of trona alone would supply the total U.S. soda ash needs for 100 years at the present consumption rate. In addition, the reserves of brine in California from which sodium carbonate, sodium sulfate, and other minerals are recovered are known to be large.

[1] Commodity specialist.

Nearly one-half of the sodium carbonate produced is required in manufacturing glass; one-quarter for chemicals; and the remainder in producing pulp, paper, soap, and detergents, in producing aluminum, for treating water, and for other miscellaneous uses. The total U.S. production of manufactured and natural soda ash is expected to increase at the anticipated growth rate of GNP or quadruple by the close of this century. The expected growth in chlorine consumption may cause an overproduction of the coproduct, caustic soda, which is a substitute for soda ash, and thus depress the demand for soda ash. However, new uses for caustic soda have absorbed and should continue to absorb the extra production of caustic.

Two-thirds of the more than 1-million-ton demand for sodium sulfate (salt cake) in the United States is supplied as a byproduct of chemical processes at 40 plants located in 16 States (12 Eastern and Southern, 3 Central, and 1 Western) that produce rayon, cellophane, hydrochloric acid, and other chemicals. The remainder comes from natural sources at three operations in California and one each in Texas and Wyoming. Four percent of the U.S. production of sodium sulfate was exported. However, imports were equivalent to 13 percent of domestic production.

The reserves of natural sodium sulfate in the Western United States and Canada exceed several hundred million tons, sufficient to supply our needs for several hundred years. In addition to the natural and byproduct sources, the raw materials from which sodium sulfate could be produced are sufficient to meet all future expanding needs. The kraft paper industry consumes more than two-thirds of the total U.S. sodium sulfate production. It is also used in making glass, ceramic glazers, detergents, stock feeds, dyes, textiles, and miscellaneous chemicals.

An anticipated increase in the demand for sodium sulfate and decline in byproduct salt cake output are expected to be supplied by natural sodium sulfate production. Consequently, a greater proportion of the total requirements should be supplied each year from natural sources.

Sodium metal is recovered by electrolysis of a fused mixture of calcium and sodium chlorides in Downs cells. Because sodium metal is extremely reactive and ignites spontaneously when exposed to air or moisture, handling, controlling reactions, and maintaining it in the required state of purity present difficulties.

Sodium metal is produced by three companies at five plants in five States. The annual output of 110,000 to 125,000 tons is used chiefly in producing tetraethyl and tetramethyl lead—two compounds added to fuels to increase their antiknock rating. This use is affected by the demand for high-test fuel, which is not required by economy cars. An increasing use of jet aircraft and gas turbines will depress this use. Metallic sodium also is used in metal descaling, ore reduction, manufacturing sodium peroxide and other chemicals, and in cooling or transferring heat in certain types of atomic reactors. New and expanded uses for metallic sodium are expected to take the places of any declining uses.

BACKGROUND

The elements sodium and chlorine are essential to animal life, and, as sodium chloride meets this requirement most readily, salt has been a dietary essential since earliest times. Early mankind depended upon the flesh of animals and the occasional outcroppings of salt or salt licks frequented by animals to satisfy his salt requirements. As civilization progressed, mankind learned to evaporate sea water and brines of saline lakes and springs to obtain salt; uses and demand for salt grew enormously; huge underground deposits now are mined on a large scale to supply most of the ever-increasing salt requirements of modern civilization.

The importance of salt in the minds of early men may be seen from the many allusions to salt found in the Bible and other historical writings. Expressions such as "not worth his salt," "the salt of the earth," and other sayings have become idiomatic in the English language. Salt has symbolized friendship, fidelity, purity, and hospitality. It has been used as a currency, has had religious significance, caused wars, and has been a favorite commodity for taxation.

Today salt retains its importance to the physical well-being of mankind, and in addition, it has thousands of other uses. Of each 100 pounds of salt produced in the United States, less than 3 pounds is for table use. The other 97 pounds is for chemical, industrial, and agricultural uses.

The history of sodium carbonate also goes back into antiquity. It was recovered by the early Egyptians from incrustations around playa lakes. Until near the end of the 18th century, seaweeds and marine plants were

burned and sodium carbonate recovered from the ashes for use in soap, cleaning compounds, and glass. From these early sources the common term of sodium carbonate became soda ash. About 1791 Le Blanc in France developed a commercial process for the production of sodium carbonate, using salt, limestone, and coal. This process was widely used in Europe. In the 1860's the Solvay brothers of Belgium developed a process for manufacturing sodium carbonate from salt, limestone, and ammonia. The Solvay process, also called the ammonia-soda process, now is used in making most of the world's sodium carbonate.

During World War I, when imports of potash and other salts were curtailed, increased attention was focused on domestic deposits of these salts, such as those at Searles and Owens Lakes in California. Besides salt, these deposits are rich in sodium carbonate and sodium sulfate, as well as compounds of potash, borax, lithium, and other minerals. The chemistry involved in separating the various products was complex; however, as the technology for exploiting these and other saline deposits improved, the production of sodium carbonate and sodium sulfate from natural sources gradually increased. The byproduct salt produced in these operations is usually wasted.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

With an annual production of nearly 31 million tons, the U.S. salt industry ranks among the largest in the nonmetals field. Salt is foremost of the mineral commodities consumed by the chemical industry. In fact, chemical concerns are among the largest producers of salt.

Salt was produced by a total of 57 companies at 95 plants in the United States in 1963. Six of the leading salt-producing companies, operating a total of 26 plants, produced 65 percent of the total output. Ten companies each produced in excess of 1 million tons. The leading 24 companies, each producing more than 100,000 tons, operating a total of 62 plants, accounted for 96 percent of the total salt output. The remaining 4 percent of the total output was produced by 33 companies at 33 plants. About two-thirds of the salt produced in the United States was recovered as salt in brine and sold or used as such.

Louisiana was the leading salt-producing State in 1963 with 20 percent of the total output; Texas was second with 19 percent; and New York was third with 16 percent. Michigan and Ohio each produced about 14 percent of the total and California 6 percent. These 6 States supplied 89 percent of the total U.S. output. The remaining 11 percent came from 12 other States.

Although domestic salt-producing areas are widely distributed, several areas are without known salt deposits or facilities that can be developed at competitive costs. Notable examples are New England and most of the East Coast States. The Pacific Northwest is an important salt-consuming industrial area lacking in local salt-producing facilities.

Canada and Mexico are the chief source of U.S. salt imports, furnishing nearly three-fourths of the total in 1963; major quantities also came from the Bahamas, Jamaica, Spain, Tunisia, and Egypt.

The United States leads the world in production of sodium carbonate with an annual output of nearly 6 million tons in 1963. By far the greatest proportion, 81 percent, is produced from sodium chloride by the ammonia-soda (Solvay) process. Eleven eastern and midwestern plants strategically situated in regard to salt and limestone deposits and nearby chemical markets provided the bulk of the Nation's soda ash requirements. The remaining soda ash output was supplied from natural sources of sodium carbonate, such as brines of Searles and Owens Lakes in California and underground deposits in Wyoming.

The growth of the sodium carbonate industry since 1960 has been largely from natural soda rather than ammonia-soda production. The high cost of new ammonia-soda plants compared with natural soda producing and refining operations probably caused the stalemate in new ammonia soda plant construction and increased interest in natural soda output. In 1962, the cost of a new 1,000-ton-per-day ammonia soda plant, the smallest that can be built and operated profitably, was estimated at $40 million.

Production of sodium carbonate and sulfate from natural sources comes from three States—California, Wyoming, and Texas. In California, both commodities are produced from the brines of Searles Lake by American Potash & Chemical Co. and Stauffer Chemical Co., West End Division. Pittsburgh Plate Glass Co. recovers sodium carbonate from brines of Owens Lake. U.S. Borax & Chemical Corp., Pacific Coast Borax Division, produces sodium sulfate as a coproduct in making boric acid from borax.

In Wyoming, FMC Corp., Inorganic Chemicals Division, and Stauffer Chemical Co. of Wyoming, West End Chemical Co. Division, operate underground trona mines near Green River and were two of the major producers of natural sodium carbonate in 1963. Plans were

made for expanding mining and processing capacities at these operations, and other firms were conducting exploration work on trona deposits in the area or contemplating installations. William E. Pratt produces sodium sulfate from semidry lakebeds near Casper, Wyo.

In Texas, the Ozark-Mahoning Co. produces sodium sulfate from brines at two operations, Monahans and Brownsville.

Production of manufactured sodium carbonate is mainly in the East and Midwest. The 11 plants are distributed in the United States as follows: 2 each in Louisiana, Michigan, Ohio, and Texas, and 1 each in New Jersey, New York, and Virginia.

Sodium sulfate output in the United States was 1.2 million tons in 1963. About 64 percent was produced as byproducts or coproducts of chemical processes that produced rayon, cellophane, hydrochloric acid, sodium bichromate, boric acid, phenols, and other chemicals; and 36 percent was produced from natural sources in California, Wyoming, and Texas.

Manufactured sodium sulfate was produced as a byproduct or coproduct at 40 plants in 16 States—12 Eastern and Southern, 3 Central, and 1 Western—in 1963.

Sodium metal is produced as a coproduct, along with chlorine, by three companies by electrolysis of molten salt at five plants in five States. E. I. du Pont de Nemours & Co., Inc., has plants at Niagara Falls, N.Y., and Memphis, Tenn.; Ethyl Corp. at Baton Rouge, La., and Houston, Tex.; and National Distillers & Chemical Corp. at Ashtabula, Ohio. The output in 1963, 125,566 tons, was used chiefly in making tetraethyl and tetramethyl lead, a gasoline additive.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Brine is a term applied to solutions of salts in water. The brines of the seas and other natural brines were formed by fresh-water leaching of rocks and soil containing soluble minerals. Natural brines usually have been concentrated by evaporation.

Artificial brines are produced by injecting fresh water into salt formations and allowing the salt concentration to build up to a point near saturation. Artificial brines used by the salt-producing industry are approximately 25 percent sodium chloride.

Evaporated salt is a term applied to fine crystals of sodium chloride produced by evaporating brines in large covered, steam-heated kettles or pans under vacuum conditions.

Solar salt is the term applied to salt crystallized in shallow ponds by exposing brines to evaporation by sun and wind. In some Bureau of Mines tabulations, solar salt is included with evaporated salt. Bittern is the concentrated solution of various salts remaining after most of the salt (sodium chloride), has been crystallized from natural brines by solar evaporation.

Highly pure evaporated salt produced in open pans either by the Alberger or Grainer process is called flake salt. It is characterized by an agglomerated crystal of flakes and cubes.

Grainer salt consists of relatively large, pure, hopper-shaped crystals and is produced primarily for the food industries' use in butter, cheese, crackers, pretzels, and other products. The crystals are caused to grow in the shape of inverted pyramids or hoppers by allowing slow evaporation at the undisturbed surface of the brine. As the brine flows slowly through long, shallow, steam-heated troughs, known as open pans or grainers, floating seed crystals grow circumferentially, gradually sinking deeper as they grow heavier, until they sink to the bottom and are collected.

Rock salt is a term applied to salt produced by drilling and blasting natural salt deposits. Salt domes are large masses or plugs of salt formed by pressure deformation of natural salt deposits.

Soda ash is the term used in the industry for sodium carbonate (Na_2CO_3). When crystallized with 10 water molecules it is washing soda. Baking soda ($NaHCO_3$) contains a greater proportion of CO_2 than soda ash. Trona or sodium sesquicarbonate ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) is a commercially important sodium carbonate mineral. Caustic soda, sodium hydroxide (NaOH), commercially known as caustic alkali, lye, or simply caustic, is recovered as a coproduct of chlorine from salt.

Solvay soda or ammonia soda are terms used interchangeably for sodium carbonate produced from salt by the Solvay process.

Light ash is soda ash having a bulk density of 32 to 35 pounds per cubic foot. Dense ash is the same material having a density about 60 to 66 pounds per cubic foot.

Salt cake is the term used for sodium sulfate (Na_2SO_4). Glaubers salt is a common hydrated form of sodium sulfate ($Na_2SO_4 \cdot 10H_2O$).

In the salt industry the quality of the product of one manufacturer usually is the same, grade for grade, as that of another. Grades usually refer to size distribution rather than quality.

Four grades of commercial salt produced at a rock salt mine operated by one of the leading salt-producing companies are as follows:

Size:	Through—	Retained on—
No. 2	0.500 inch	0.420 inch.
No. 1	0.420 inch	0.301 inch.
Coarse C	0.301 inch	10-mesh.
Fine C	10-mesh	None.

Rock salt produced in the United States usually has a sodium chloride content above 98 percent. Impurities are chiefly calcium and magnesium sulfates and chlorides. Evaporated salt from vacuum pans usually contains less than 0.5 percent impurity; flake and grainer salt usually contain less than 0.2 percent impurity.

Many specialty salt products contain special additives. Caking due to moisture absorption in table salt is retarded by adding 0.5 to 2.0 percent of an additive such as magnesium carbonate, calcium carbonate, hydrated calcium silicate, or tricalcium phosphate. These additives often are referred to as fillers or driers. To be effective they must coat each salt crystal and not become dusty.

Iodized salt contains 0.01 percent potassium iodide and a stabilizer consisting of 0.1 percent sodium carbonate and 0.1 percent sodium thiosulfate or other suitable nontoxic stabilizing agents. Iodized table salt is an effective means of preventing certain diseases attributed to iodine deficiency in the diet.

For salting livestock, fine particles of either evaporated or rock salt are compressed into 50-pound blocks, 4-pound bricks, or 3-ounce pellets. In addition to plain salt the blocks are made with the following additives: (1) 2 to 4 percent sulfur; (2) 0.01 percent potassium iodide; (3) trace minerals including compounds of manganese, iron, cobalt, copper, iodine, and zinc; and (4) minerals such as carbonates and phosphates.

"Federal Specification SS–S–31h, June 25, 1964, Salt: Table," approved by the Federal Supply Service, General Services Administration, covers specifications for table salt, plain or iodized, for use by the agencies of the Federal Government and are not otherwise binding on industry. However, the products marketed by the industry for use in food meet or exceed these specifications for table salt, which are set forth as follows: Table salt shall be of edible grade, clean, sound, wholesome, and free from extraneous matter. Plain table salt shall be free flowing and shall be derived from fine granulated salt (rock salt) or evaporated salt, with one or more effective anticaking agents. The plain table salt shall contain not less than 97.5 percent sodium chloride on a moisture-free basis and not more than 0.1 percent moisture. When fine granulated salt is used, table salt shall be of such size that not less than 95 percent shall pass through a U.S. Standard No. 25 sieve and not more than 10 percent shall pass through a No. 70 sieve. When evaporated salt is used, table salt shall be of such size that 100 percent shall pass through No. 16 sieve, and not more than 20 percent shall pass through a No. 100 sieve. If iodized salt is specified, the iodized salt shall conform to the finished product requirements of plain salt. In addition, the iodized salt shall contain potassium iodide not less than 0.009 and not more than 0.01 percent or other nontoxic iodine compounds with a stabilizer consisting of sodium carbonate or sodium thiosulfate or other suitable stabilizing agents which are equally effective in preventing the loss of iodine.

"Federal Specification SS–S–550, July 5, 1957, Sodium Chloride, Technical, for Water Softening Units," covers salt for use in regeneration of water-softening units by the agencies of the Federal Government. Type I rock salt shall pass through a ⅜-inch sieve and at least 95 percent shall be retained on a No. 60 sieve. Minimum sodium chloride shall be 97 percent, maximum moisture 0.50 percent. Type II, grade A, evaporated salt shall pass through a ⅜-inch sieve and not more than 5 percent shall pass through a No. 100 sieve. Sodium chloride shall be at least 98 percent, and moist shall not exceed 0.50 percent.

TECHNOLOGY

Salt

The technology of salt production, properties, and uses have been described in a comprehensive publication (*19*).[2] Papers presented in five principal areas of salt technology—geology of salt formations, mining rock salt, evaporated salt, solution mining, and underground storage—were published in a major source book on both salt technology and North American salt deposits (*1*).

Sodium chloride has a molecular weight of 58.454 and contains by weight 39.34 percent sodium and 60.66 percent chlorine. It has a hardness of 2.5 and a specific gravity ranging from 2.1 to 2.6 for rock salt and 2.165 for the pure crystal. Salt is transparent or translucent and highly diathermic. When pure it ranges from white in the finely divided state to gray in large masses. Salt has a vitreous luster.

Traces of iron oxides in salt produce various shades of yellow, orange, brown, pink, or red. The peculiar shade of red sometimes found in salt produced by solar evaporation of sea water has been attributed to tiny organisms. Blue mottlings sometimes seen in halite crystals have been attributed to colloidal sodium.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

Salt is soluble in water to the extent of 35.7 parts per 100 parts of water at 0° C and 39.8 parts per 100 of water at 100° C. The small difference in solubility due to temperature changes is an important factor in the economics of producing salt by evaporating brine. Salt has a negative heat of solution, which is 1,281 kilogram-calories per mole at 18° C in 200 moles of water. This energy value is an important factor in the cost of freshening salt water.

Under great pressure, rock salt is plastic and will flow slowly as a viscous fluid. The viscosity of rock salt is 10^{18} poises at 18° C and 10^{17} poises at 80° C. For comparison, the viscosity of asphalt is 10^{7} poises at 20° C. The ability of rock salt to flow under pressure enables it to seal cracks and fissures in the surrounding rock, helping to keep the interior of salt mines dry. This property also permits the formation of salt domes.

Salt is found in two forms—solid, as rock salt, and in solution, as brines. The salt content of the seas is attributed largely to leaching of soluble salts from rocks and soil by water resulting from precipitation. Some of this water flowing through streams eventually reaches the sea. Many rivers have an appreciable salt content and because of their volume pour large quantities of salt into the oceans (*23*). For example, it is estimated that the Rio Grande deposits 5 tons of salt in the Gulf of Mexico each minute. As water evaporates from the sea surface the salts remain in the brines. The average concentration of salts in sea water is about 35 grams per liter. More than 40 different molecular and ionic substances have been detected in sea water, but three-quarters of the total dissolved solids is sodium chloride (*7, 34*).

As evaporation of sea water approaches completion, the brine becomes saturated with respect to the various salts at different stages. Knowledge of the order of precipitation of salts from sea water helps to explain how relatively pure sodium chloride may be deposited from sea water containing many different salts.

The following order of deposition of salts from sea water occurs: (1) Fe_2O_3 and $CaCO_3$ were precipitated as the brine was evaporated to 53 percent of its original volume; most of the $CaSO_4$ and the remainder of the $CaCO_3$ were precipitated as the volume was reduced further to 19 percent. Sodium chloride began to precipitate when the volume reached 9.5 percent and the density 1.21 and continued until the solution was dry. Small quantities of $CaSO_4$, $MgSO_4$, and $MgCl_2$ were deposited along with the salt until the volume was reduced to 3.90 percent, at which point some NaBr was also precipitated until the density reached 1.32 and the volume was 1.66 percent of the original. From this point on further evaporation precipitated potassium chloride and a series of complex salts, the composition of which depended on the temperature and the relative concentration of the salts remaining in the mother liquor. The potash deposits of Carlsbad, N. Mex., have been attributed to the precipitation of the mother-liquor salts in the final stages of the evaporation of a Permian Sea. The Stassfurt deposits are believed to have a similar origin.

Under certain conditions a body of sea water may become isolated from the circulating ocean currents by a reef, sandbar, or other means; and under suitably dry and warm climatic conditions the evaporation proceeds until the salts are partially or entirely deposited. With continuous or periodic influx of sea water to replace evaporation, large deposits of salt have been built up—in some instances several thousand feet in thickness. Deposits of this type have been called lagoonal. During the Permian age two famous salt deposits of the lagoonal type were laid down—one in northern Germany and the other in eastern New Mexico. A second large bedded deposit in the United States is the Silurian salt deposit, which underlies Michigan, New York, Pennsylvania, Ohio, and West Virginia. It was formed in much the same manner as the Permian beds by the evaporation of a large inland sea known as the Silurian Sea, which became separated from the ocean and gradually evaporated. As no mother-liquor salts were precipitated it is assumed that evaporation was never completed.

Playa deposits are formed by leaching of surrounding sediments, followed by the evaporation of the water leaving the salts. The composition of the brines and salt beds of these deposits generally do not resemble sea water; those of California and Nevada contain in addition to sodium chloride much carbonate, sulfate, and potash as well as appreciable percentages of boron.

Salt domes are large vertical structures of salt, resulting from deformation of bedded salt deposits under great pressure. The plastic nature of halite and its low density, compared with the surrounding rock, permits deeply buried sedimentary deposits to be forced upward through zones of weakness in the overlying rocks, forming vertical columns or domes of salt extending several thousand feet in height and cross section. If the bedded deposit at the base of the dome is sufficiently large, the salt columns may rise to the surface. Surface features may or may not indicate the presence of underlying salt domes; most have been detected by geophysical methods and proved by drilling. There are 300 salt domes reported to exist in the gulf coast area from Alabama to Mexico.

In addition to those of the gulf coast area, salt domes have been found in other parts of the world, notably in Colombia, East and West Germany, Spain, Rumania, Egypt, Algeria, Morocco, Iran, and U.S.S.R.

Production Methods

Salt is produced in three ways: (1) By solar evaporation of sea water, lake, and other brines; (2) by room-and-pillar mining of bedded and dome deposits similar to mining coal; and (3) by solution mining methods in which water is injected into the salt deposit, forming an artificial brine, which is pumped to the surface, where the salt content is utilized.

Throughout the world, solar evaporation is the most widely used of the three methods because of its simplicity. However, in the United States, because of climate and other factors, less salt is produced by solar evaporation than by either of the other two methods. Solar salt is produced in California, Hawaii, Nevada, New Mexico, and Utah by highly mechanized processes best exemplified perhaps by the operation of the Leslie Salt Co. on the southern shores of San Francisco Bay (*39*). Here are found all factors necessary for an economically successful solar plant: (1) Large areas of low-lying flatlands, (2) a clay subsoil, which quickly becomes impervious to brines, (3) low rainfall, (4) high net evaporation, (5) drying winds, (6) comparatively long seasons free from precipitation, and (7) nearby markets.

A salt "farm" consists of concentrating ponds and crystallizing ponds. The ratio of the area of these types of ponds is approximately 15 : 1. A unit often consists of 9 or 10 concentrating ponds and several crystallizing ponds. The No. 1 concentrating pond is flooded with sea water in the fall, usually by opening floodgates at high tide. As evaporation increases the density of brine, initially about 3.0° Baumé, the brine is pumped successively through the various ponds, taking advantage of the forces of gravity and prevailing winds where possible until it reaches 26.0° Baumé and is saturated with sodium chloride (NaCl) In the early concentrating stages, most of the calcium and iron compounds precipitate and the brine then goes to the crystallizing pond where it is further concentrated to 29.0° Baumé.

In the concentration range between 26° and 29° Baumé, virtually nothing but sodium chloride is deposited to a depth of 4 to 6 inches on the flat, smoothly rolled bottoms of the ponds. As further concentration of the brine causes excessive crystallization of magnesium salts, the remainder of the brine (bittern) is either wasted or sold for the recovery of magnesium and bromine.

The salt is harvested each year before the autumn rains begin by specially designed tractor-mounted machines, which break up the salt with horizontally mounted revolving picks. A short conveyor delivers the salt to hopper cars, which carry it to the washer. After washing with saturated brine, followed by a fine spray of fresh water, the salt is stockpiled in the open. A hard crust soon develops protecting the pile from rain loss, estimated to be only 5 or 10 percent. Five to 7 years is normally required to bring a pond to full production, which is about 40 tons per acre in this area. Most of the salt is marketed as undried crude 99.4 percent NaCl, and the remainder is kiln dried, 99.8 percent NaCl, and vacuum refined salt with a purity of over 99.9 percent NaCl.

Rock salt is mined on a large scale in Michigan, Texas, New York, Louisiana, Ohio, Utah, New Mexico, and Kansas (*3, 4, 33*). The room-and-pillar method is used principally. Rooms tend to be large but vary in size in different mines, depending on the thickness of the seam and other factors. In the Retsof mine near Rochester, N.Y., a 9½-foot seam is mined at a depth of about 1,000 feet. Rooms are 63 feet wide and about 500 feet long. Pillars are 57 feet wide and alternate 185 and 220 feet long. This system permits removal of 70 percent of the salt, leaving 30 percent in the pillars. The mined-out area of the Retsof mine is approximately 1,600 acres, making it the largest salt mine in the Western Hemisphere (*29*). In dome-type deposits, such as those of Louisiana, the rooms may be more than 100 feet high.

Unlike most mines where the desired mineral is a comparatively small seam mixed with and surrounded by gangue material, a salt mine is usually completely enclosed in salt. The nature of the material is such that the roof between pillars is self-supporting, and no timbering is required. Moisture on the outside of the salt body tends to form a crystallized crust, which protects the interior of the body from moisture and seepage.

Salt mining is similar to coal mining and is highly mechanized. In one mine an undercutter cuts a slot 10 feet deep at the base of the wall, which is then drilled and blasted. About 0.4 pound of dynamite per ton of salt is required. To eliminate copper contamination of the salt, aluminum blasting caps and iron leg wires are used. Pieces of the wire are later removed magnetically. The broken salt is loaded mechanically into cars or trucks and hauled to an underground crusher. Belt haulage has proved satisfactory in some mines following the devel-

opment of a portable crushing machine, which reduces the lumps to a size that the belts can handle. At the surface the salt is crushed, screened, graded, and made ready for the market.

Bench mining of rock salt in a massive Louisiana salt dome successfully overcame problems of the conventional face drilling system. A 50-foot-wide bench was prepared by drilling a row of seven vertical holes 8½ feet back from the face of the bench. The holes were drilled to a 34-foot depth, allowing 4 feet to collect cuttings not cleaned from the hole. After undercutting through the holes with a shortwall cutter having a 9-foot bar, the holes were charged with a 60-percent strength semigelatin explosive. A typical blast, requiring 186 pounds of explosive, broke about 900 tons of salt ready for loading. (*17*, *43*).

Ammonium nitrate-fuel oil mixtures are used as a blasting agent in several large rock salt mines (*30*). Fuel oil, amounting to 6 percent of the weight of ammonium nitrate, was added to plastic bags of ammonium nitrate prills, and the bags allowed to stand 24 to 48 hours before being placed pneumatically into the hole.

About two-thirds of the U.S. salt output is produced by introducing water into a cavity in the salt deposits and removing the brine. This procedure is relatively simple and has particular advantage when the salt is to be used as a brine as, for example, in chemical uses such as soda ash and caustic manufacture. Holes are drilled through the overburden into the deposit and cased with iron pipe. Water is introduced into the deposit through a smaller pipe inside the casing. A nearly saturated brine is formed in the cavity at the foot of the pipe. This brine is pumped or airlifted through the annular space between the pipes. Numerous techniques have been developed to control the shape of the cavity so that a saturated brine will be formed and eventual subsidence and caving of the cavity will result in the least damage to the well. Most of these techniques involve positioning of the water intake and brine exit pipes in the cavity and the employment of a cushion of air to control the degree of contact between solvent and salt formation. After adjacent wells have been operated 1 or 2 years, their cavities may become connected. When this occurs the usual practice is to introduce water into one well and remove brine from the other.

In recent years hydraulic-fracturing techniques to form channels between wells, developed by oil producers to increase output, were adapted to solution mining of salt with great success and increased efficiency. In this system a series of wells drilled to the base of a salt formation are caused to interconnect by injecting water under high pressure into one of the wells and continuing to pump water into the well until a fracture occurs to a nearby well or wells. In mining, fresh water is introduced in one string and saturated brine is removed from the other (*13*).

The cavities developed in salt mines both by dry mining and solution mining techniques have been found to be admirably adapted as storage vaults. Rock salt has strength enough to support itself over moderate spans without danger of collapse. Salt formations have good thermal conductivity and are relatively impervious to seepage of water, so the cavities have an even temperature and relatively low humidity. Principal rock-salt areas in the United States have a good record of earthquake stability. Storage of petroleum products and radioactive wastes in salt cavities is said to be economical and safe (*31*). Many physical and chemical properties of salt beds are well adapted to storage of hot chemical materials in liquid form. Tests made in the Carey Salt Miles at Hutchinson, Kans., were described (*18*).

As a part of a program to explore the peaceful uses of nuclear energy, the Atomic Energy Commission triggered a nuclear device in a cavern created in a salt dome near Carlsbad, N. Mex. The design, methods, and costs of sinking the Gnome shaft to set the charge were described (*16*, *37*).

Preparation for Market

Mined rock salt usually receives no treatment other than crushing and grading. Treatment of brine varies, depending on the impurities present. Some brines are acidified, aerated, treated with chlorine, and clarified to remove traces of hydrogen sulfide and iron before being delivered to the soda plant or the evaporator.

Evaporated salt is salt produced from brines, either natural or artificial. In table 1 evaporated salt includes all salt produced by solar evaporation as well as evaporation by the use of fuel. The category "in brine" refers to the salt content of brines produced and used as such.

The two main types of evaporators used by the salt industry are vacuum pans and graniers. The first produces the fine granulated cubic crytals of salt familiar to all of us; the second produces larger hopper-shaped crystals required in the processing of foods, particularly cheese and butter, and for other uses requiring a high rate of solubility.

Most evaporated salt is a product of the vacuum pan, a large cylindrical vessel, which

may be 18 feet in diameter and 60 feet high, with a conical top and bottom. In older models, steam-heated calandria encircles the vessels just below the midsection, and a large impeller helps to circulate the brine upward through the tubes of the heater and down through the center downtake. Crystallized salt collects in the conical bottom and is removed as a slurry. The pans are operated under partial vacuum to take advantage of reduced boiling temperature of the brine under lower pressure. In newer models, the brine is heated by circulating through a heat exchanger outside the main body of the evaporator.

Economy is substantially increased by operating several of the pans in series, using the vapor produced in one pan to heat the brine in the next; each succeeding pan operates on a slightly higher vacuum. This is known as multiple-effect evaporation, and three or four effects are common in the salt industry.

Over the years many improvements both in the design and operation of vacuum pans have been evolved. Calcium sulfate scale, which formerly crusted the heat-exchange tubes of the calandria and had to be drilled out each week, is no longer a problem. Scaling is now largely controlled by maintaining a certain concentration of fine calcium sulfate crystals in the evaporator brines. The dissolved calcium sulfate, which tends to precipitate in the pans as the temperature increases, is thus provided with small, circulating nuclei on which to grow, and the heating tubes are not encrusted. The slurry of salt crystals and brine emerging from the evaporator is washed with a saturated salt solution to remove fine particles of both calcium sulfate and salt. These are recycled to the evaporator.

A second problem encountered in vacuum evaporators is that of "salting" or encrusting the heating surfaces with cakes of salt. The remedy for this situation is believed to be in higher velocities and heavier slurries of salt in the pans.

Because of the corrosive nature of salt, the older pans of cast iron with copper heating tubes are gradually being replaced with pans of more resistant alloys such as monel. This not only permits longer useful life for the equipment, but also causes less contamination of the salt. These large, expensive machines are a factor in the high investment costs of the salt industry (*44*).

Because of the demand by the food-processing industries for salt having the characteristic hopper-shaped crystal produced in grainers, these rather inefficient evaporators are still in use. Grainers are shallow troughs up to 120 feet in length in which brine is heated by steam pipes. Evaporation takes place at the surface where the crystals first form and float, growing circumferentially and finally sinking to the bottom, where they are collected by mechanical rakes.

As grainers are essentially single-effect evaporators their steam economy is low. Several improvements have been proposed, based on the principle of flash evaporation. The Alberger process is one that has been used for a number of years. The product, a flake salt, can be substituted for grainer salt in many applications, except where large crystals are needed, such as in curing hides and salting fish.

A new process for producing highly pure evaporated salt assaying 99.99 percent NaCl employing a double-effect evaporator was developed and placed in operation (*9*). This method uses the recrystallizing process and utilizes the excessively fine low-grade rock salt, which may exceed 15 percent of the total output of a mine (*35*). Compacting machines for agglomerating rock salt fines were developed. The preheated fine salt was fed between spring-loaded rotating rolls and emerged as a continuous ribbon of salt, which was broken into granules and screened to produce the desired size (*20*).

A new method of solids separation having particular application to upgrading rock salt was patented and its development was described (*6*). This thermoadhesive method is based on the greater transparency of sodium chloride crystals to infrared radiation, compared with such typical impurities as anhydrite, dolomite, and shale. Under infrared radiation the impurities are selectively heated more than the salt crystals. The irradiated impure salt is then spread evenly on a high-speed conveyor belt with a heat-sensitive surface. When the belt rounds the head pulley the cooler rock salt particles are thrown further forward than the impurities, which stick to the belt, and a concentration is achieved.

Sodium Carbonate

Sodium carbonate is a very soluble salt found naturally in certain spring and lake brines and in deposits formed by evaporation of similar brines. Trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) is the most common sodium carbonate mineral found in nature. It crystallizes from solution when carbon dioxide gas is bubbled through solutions of sodium carbonate having a concentration greater than 9 percent. Carbonation of less concentrated solutions precipitates sodium bicarbonate.

Among the less common minerals containing sodium carbonate are the following: natron,

$Na_2CO_3 \cdot 10H_2O$; thermonatrite, $Na_2CO_3 \cdot H_2O$; nahcolite, $NaHCO_3$; burkeite, $2Na_2SO_4 \cdot Na_2CO_3$; hanksite, $9Na_2SO_4 \cdot 2Na_2CO_2 \cdot KCl$; northupite, $MgCO_3 \cdot Na_2CO_3 \cdot NaCl$; personite, $Na_2CO_3 \cdot CaCO_3 \cdot 2H_2O$; gaylussite, $Na_2CO_3 \cdot CaCO_3 \cdot 5H_2O$; and shortite, $Na_2CO_3 \cdot CaCO_3$ (*22*, *38*, *40*).

The largest known deposit of relatively pure sodium carbonate mineral in the United States was discovered in Wyoming in 1938. While drilling for oil near Green River, a bed of trona was penetrated at a depth of about 1,500 feet. Further test drilling revealed a horizontal trona deposit in the Green River formation resulting from the evaporation of an ancient lake. The deposit is relatively free of chlorides and sulfates and contains 5 to 10 percent insoluble matter (*14*, *28*).

In 1947 the Intermountain Chemical Co., an affiliate of Food Machinery & Chemical Corp., sank a 12-foot-diameter, concrete-lined shaft to the Wyoming deposit and began mining trona. Since then a modern mine and treatment plant have been constructed. A 10-foot seam of trona is mined at a depth of 1,500 feet by the conventional room-and-pillar system with total pillar recovery. Rooms are 8 feet high, 20 feet wide, and 250 feet long on 65-foot centers. Continuous miners (machines) have been used, but the hardness of the trona reduced the speed of advance to one-fourth the rate in coal (*8*, *15*).

From the face, the broken trona is loaded on cable-reel shuttle cars by conventional coal-loading machines, which have been reinforced to cope with the heavier and more abrasive trona. Two shuttle cars normally operate between the working face and the main haulage conveyor belt. All mobile equipment is mounted on rubber tires. Balanced skips in a two-compartment shaft hoist 3,000 tons of trona per day to the surface processing plant.

Laminated shales of little inherent strength lie above the trona bed, posing a problem of roof support. After studying various methods, roof bolts were adopted as the standard roof support.

Directly beneath the trona lies an oil shale that is subject to heaving. Floor heaving continues to be a problem in this mine.

In theory, a ton of pure trona is convertible to 0.704 ton of sodium carbonate by calcination driving off water vapor and carbon dioxide. However, in practice, trona is usually dissolved and recrystallized, eliminating many insoluble impurities and permitting recovery of sodium carbonate crystals of the desired form. The surface refining plant of the Intermountain Chemical Co. requires about 2 tons of crude ore for 1 ton of finished sodium carbonate.

Mining operations at the Big Island trona mine of Stauffer Chemical Co. near Green River, Wyo., were begun in 1962 (*5*). Two circular, cement-lined shafts were completed to the lower of two minable trona beds. The service shaft was 830 feet deep and the ore shaft 930 feet below the surface.

The designed daily capacity of the mine, using conventional room-and-pillar mining, was 1,200 tons of ore, averaging 90 percent trona. Thirty-five percent of the ore was left behind in supporting pillars.

All equipment was operated electrically except for one diesel-powered shuttle car. The mining cycle was begun by cutting a narrow slot 10 feet deep at the top of the working face. After drilling the face and blasting with ammonium dynamite, the broken ore was loaded mechanically into rubber-tired shuttle cars and carried to the main-haulage conveyor belt. At the end of the conveyor, before being hauled to the surface, the ore passed through a 24- by 60-inch single-roll crusher which reduced the size of the lumps to minus 5 inches.

The back was supported by roof bolts 54 and 60 inches long placed on 4-foot centers. Mine openings were 9 to 10 feet high and 16 feet wide. Three to four feet of trona were left in the back for support, as the marlstone and shales surrounding the trona are unstable.

Proper ventilation and other precautions necessary in a gassy mine were required because of the presence of methane in the surrounding shales.

Discovery of superheated brines rich in minerals created considerable interest among chemical and power producers in the Salton Sea area of southern California. Five wells were drilled in an effort to develop geothermal power known to be a possibility in the area. Unexpectedly high concentrations of minerals found in the brines were believed to improve the economic feasibility of a combined chemical and power producing project. The brine from one well flowing at 280,000 pounds per hour at 199°C had the following concentrations in parts per million: Sodium, 70,000; calcium, 34,470; potassium, 24,000; iron, 4,200; borax as B_4O_7, 537; lithium, 150, and chlorine, 201,757. Although the economic potential of the brines was supposed to be high, their utilization depended upon developing an economically feasible scheme for extracting and processing the minerals into commercial products.

In California, sodium carbonate is produced from the complex brines of Owens Lake and Searles Lake by processes involving carbonation, evaporation, and cooling. In the plant completed in 1958 by Columbia Southern Corp. and operated by Pittsburgh Plate Glass Co.,

Chemical Division, since 1960, saturated brines of Owens Lake are pumped into tall carbonating towers, where trona crystals form under carefully controlled conditions. The crystals are separated from the mother liquor, washed, dried, and sold as technical-grade sesquicarbonate. Various grades of sodium carbonate also are prepared by further refining and calcining the crude sesquicarbonate.

Two processes are used to recover sodium carbonate from Searles Lake brines. One employs carbonation of the brines precipitating sodium bicarbonate, which is dried and calcined. The other employs evaporation to precipitate the double salt burkeite ($Na_2CO_3 \cdot 2Na_2SO_4$) which is redissolved and reevaporated in the presence of NaCl. When this solution cools, glaubers salt crystals are formed and separated from the mother liquor. Further cooling produces crystals of sal soda ($Na_2CO_3 \cdot 10H_2O$). On heating, they melt in their own water of crystallization and are evaporated to produce the monohydrate, which on calcination produces the desirable dense soda ash of commerce.

Most of the U.S. soda ash consumption is produced by the Solvay or ammonia-soda process. The raw materials are salt and limestone; ammonia, required as an intermediate in the process, is nearly all recovered and recycled.

Plants are situated near abundant supplies of salt, as about 1.7 tons is required on a practical basis for each ton of sodium carbonate produced. In most instances, salt in the form of brine is produced by pumping water into wells drilled into salt formations and removing the saturated brine.

The brine is passed first to ammoniating towers where it is saturated with ammonia gas, then to carbonating towers where ammonium bicarbonate is formed. A reaction between the ammonium bicarbonate and salt produces sodium bicarbonate, which precipitates and is filtered off. Drying and calcination convert the bicarbonate to sodium carbonate, liberating carbon dioxide, which is reused. The ammonium chloride remaining in the solution after the sodium bicarbonate is removed is treated with lime and heated, driving off ammonia, which is returned to the system. Calcium chloride, largely a waste product, is formed. The reactions may be expressed by the following equations:

$$NH_3 + H_2O \rightarrow NH_4OH.$$
$$NH_4OH + CO_2 \rightarrow NH_4HCO_3.$$
$$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl.$$
$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2.$$
$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2.$$

Sodium Sulfate

Sodium sulfate minerals occur in natural brines and in solid masses in playa lakes and among sedimentary rocks. Because the minerals are quite water soluble, solid deposits and concentrated brines are usually found in areas with little drainage and a dry climate.

The principal sodium sulfate minerals are thenardite (Na_2SO_4), mirabilite or glauber salt ($Na_2SO_4 \cdot 10H_2O$), and glauberite ($Na_2SO_4 \cdot CaSO_4$). Other minerals containing sodium sulfate are glasserite ($3K_2SO_4 \cdot Na_2SO_4$), blodite ($MgSO_4 \cdot 2Na_2SO_4 \cdot 4H_2O$), hanksite ($9Na_2SO_4 \cdot Na_2CO_3 \cdot KCl$), and burkeite ($2Na_2SO_4 \cdot Na_2CO_3$) (*41*).

One theory of the formation of natural sodium sulfate involves a reaction between gypsum and bentonitic shales. Exchange of the calcium ion of the gypsum with the sodium ion of the bentonite produces sodium sulfate, which dissolves in ground water. Eventual evaporation of the water leaves sodium sulfate deposits.

The effect of temperature on the solubility of sodium sulfate in water plays an important part in its production and purification. The solubility of mirabilite increases as temperature increases up to a temperature of 32° C (90° F). Above this temperature thenardite becomes the stable solid phase, and the solubility of this salt is inversely related to the temperature.

Because of the inverse solubility-temperature relationship of sodium sulfate above 32° C, dehydration of the crystals by heat is attended by buildup of scale on the heat-transfer surfaces, making the process inefficient. Some success is claimed for submerged combustion in this difficult operation.

On the other hand, advantage may be taken of the direct solubility-temperature relationship of mirabilite below 90° F to cause crystallization of the salt from brines merely by chilling. Sometimes the brines are sprayed into the air or pumped into shallow surface ponds during the winter months when temperatures are low enough to cause crystallization of mirabilite. These crystals are gathered and dehydrated in preparation for marketing. This method, known as brine pumping, is used in mining and processing natural deposits in Saskatchewan (*24*).

Sodium sulfate is derived from natural brines and also from byproduct liquors produced in several chemical processes. For many years the chief source of byproduct salt cake was the Mannheim furnaces for producing hydrochloric acid (HCl) from salt and sulfuric acid according to the equation $2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$. Although still an important source,

newer methods of producing HCl, such as from organic chlorination processes, have reduced the market for Mannheim acid and have threatened to render the Mannheim furnaces obsolete.

Another important source of salt cake is the rayon industry. Less important sources of salt cake are the bichromate, phenol, boric acid, lithium carbonate cellophane, and formic acid industries.

Sodium Metal

Metallic sodium is a silvery white, reactive metal found in nature only in combined form. The process of electrolyzing fused sodium chloride to produce sodium and chlorine is so efficient that sodium is among the cheapest of the nonferrous metals.

Sodium reacts violently with water, producing sodium hydroxide and hydrogen, which may be ignited by the heat of the reaction. Moist air causes rapid oxidation of the metal, which must be stored in sealed containers or under a liquid such as kerosene with which it does not react.

Sodium has a specific gravity of 0.97, is malleable and soft enough to be cut with a knife, and has a high heat-transfer coefficient. Sodium has a relatively low melting point (98° C), a high boiling point (883° C), good thermal stability, low neutron-absorption cross section, and does not corrode stainless steel. These qualities have led to its use as a coolant and heat-transfer substance, particularly for nuclear reactors.

Virtually all sodium produced in the United States comes from Downs cells, an arrangement wherein sodium chloride is fused and electrolyzed, yielding chlorine at the anode and sodium at the cathode. Enough calcium chloride is added to the bath to lower the melting point of the bath from 800°C to the range 575° to 585°C (*32*).

Sodium is a powerful reducing agent, and its usefulness has been increased in recent years by the use of sodium dispersions, which are finely divided sodium particles suspended in a nonreactive fluid. Better control and efficiency in sodium reactions results from the use of sodium in this form.

Tetraethyl and tetramethyl lead additives to automotive fuels are produced commercially by reacting a lead-sodium alloy with ethyl chloride.

USES

Salt

In the United States the greatest consumer of salt is the chemical industry, which used 65 percent of the salt produced in 1963. Chlorine-caustic production alone, by electrolysis of brine, absorbed about 39 percent, and soda ash, historically the greatest single consumer of salt, took 21 percent. All other chemical uses consumed 5 percent. Much of the salt used by the chemical industry is consumed as brine.

Salt used on roads to melt ice and snow and to stabilize dirt roads consumes an important tonnage, as shown by the quantities used by State and local governments. This use of salt is one that has shown remarkable growth in recent years. This use accounted for 13 percent of the total salt output in 1963, compared with 8 percent in 1958. However, criticism has been expressed because of the corrosive effect it has on vehicles.

Large quantities of salt are consumed in the growing and processing of food. Meatpackers and tanners are foremost users in this field, as well as feed dealers and mixers. The canning, baking, fishing, dairy, and other food-processing industries also consume large quantities of salt.

An important and growing use of salt is in the regeneration of water softeners using the ion-exchange principle. Salt is also used in textile dyeing, soapmaking, pulp and paper manufacturing, metallurgy, ceramics, rubber, icemaking, and oil refining.

It may be assumed that salt sold to grocers is principally used as table salt. Although this use is the most commonly known one, it takes only about 3 pounds per 100 pounds used. Personal requirements for salt, exclusive of that used in processing food, vary but average between 10 and 17 grams or 0.3 and 0.5 of an ounce a day per person.

Salt has been suggested as a carrier of various food supplements to combat dietary deficiencies. In addition to the iodine supplement, which has gained wide acceptance, the inclusion of many of the vitamins and minerals including fluorides has been suggested. Official sanction by the Food and Drug Administration has been withheld in view of the supplements added to bread and other food products.

Less refined salt products containing calcium, and many other minerals have been used by certain populations for generations and no doubt have contributed to the dietary need for these minerals.

Sodium Carbonate

Sodium carbonate is used in the production of many organic and inorganic chemicals such as sodium tripolyphosphate (a detergent ingredient), sodium silicates, sodium bicarbonate, and lime soda caustic. This use in producing

chemicals accounted for 26 percent of the total U.S. sodium carbonate output in 1963.

Forty-four percent of the total output in 1963 was used in the glass industry to react with the glass sand, lime, and other ingredients of the melt, which on cooling and solidifying becomes the familiar glass of commerce. Bauxite is digested with sodium carbonate solution producing soluble sodium aluminated, which is hydrolyzed to produce alumina. However, many alumina plants use caustic soda, at others either caustic soda or soda ash can be used. Sodium carbonate is used in the metallurgy of other nonferrous ores, including some uranium ores. Sodium carbonate is also used in manufacturing paper. Smaller quantities of sodium carbonate are used in cleaners, water softeners, soap, and miscellaneous applications.

Two formerly important uses of sodium carbonate in which consumption has been decreasing are in the manufacture of caustic by the lime-soda process and in the production of sodium bicarbonate.

Sodium Sulfate

The kraft paper and paperboard industry requires an estimated 70 percent of the total sodium sulfate output in the United States. Salt cake aids in digesting pulpwood by dissolving the lignin, and releasing the cellulose fibers, which are processed into various paper products. In the cooking process a portion of the sodium sulfate is reduced to sodium sulfide.

Much of the salt cake is recovered and recycled, but in order to replenish losses, 175 to 200 pounds of the salt is required per ton of pulp, depending upon the type of wood being pulped and other factors.

Up to one-half of the total alkali content of glass batches may be introduced as sodium sulfate, although 5 percent for fining and scum prevention is normal. Excessive quantities increase the temperature requirement and may damage furnace refractories.

Other uses of sodium sulfate are as a filler in synthetic detergents, for stockfeed, in medicinals, textiles, dyes, and ceramic glazers, and in producing miscellaneous chemicals.

Sodium Metal

Metallic sodium is used chiefly in producing tetraethyl lead (TEL) and tetramethyl lead (TML), two compounds added in small quantities to motor fuels to increase their antiknock characteristics. Other primary uses of metallic sodium include metal descaling, ore reduction, and manufacture of sodium peroxide, hydride amide, cyanide, borohydride, and other chemicals.

The properties of sodium have become recognized in the field of heat transfer. Sodium is used to cool the valves in some internal combustion engines and for removing the heat from atomic piles.

Liquid sodium has several potential advantages as a nuclear reactor coolant. It has excellent heat-transfer characteristics; it boils at a high temperature, enabling the production of high-temperature steam without coolant pressurization; and it does not react with uranium. Among the disadvantages of liquid sodium are its chemical reactivity, particularly with water and oxygen, and the radioactivity of the sodium isotope created by neutron bombardment. As more reliable equipment for handling high-temperature molten sodium is developed, its use probably will be extended.

An experimental sodium reactor has operated successfully at Santa Susana, Calif., producing 6,000 kw for commercial distribution (*12*). Two much larger, sodium-cooled, graphite-moderated, prototype powerplants reached their designed power levels in 1962 and 1963, respectively. One is a 75,000-kw powerplant at Hallam, Nebr., and the other is a sodium-cooled, fast, neutron type at Lagoona Beach, Mich., rated at 60,900 kw. Each of the two larger reactors utilized about 300 tons of pure sodium to begin operation. Subsequent requirements are for replenishing losses, which are not large.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Byproduct salt is recovered during the concentration of calcium chloride brines resulting from soda ash manufacture. Salt is also produced by the use of sodium to reduce metallic chlorides such as titanium tetrachloride ($TiCl_4$) and as a byproduct in the manufacture of various organic and inorganic chemicals. These production methods are comparatively recent and result from the growth of the chemical industry.

Sea water, certain natural brines, and salt deposits contain various minor minerals, which, under proper conditions, may be recovered at a profit. Among these are bromine, calcium chloride, and magnesium compounds. Methods suggested for recovery of the mineral from the seas were reviewed and analyzed (*7*, *34*).

The potash deposits of New Mexico contain salt, which is separated from the potash. Some of this salt is sold. On the other hand, in the recovery of minerals from Searles Lake brines the salt content is wasted (*39*).

As most of the sodium sulfate produced in the United States is a byproduct or coproduct of certain commodities, such as rayon and HCl, any fluctuation in the production of these commodities immediately affects sodium sulfate production. In turn, sodium sulfate demand is influenced by the demand for paper and paper products. The producers of natural salt cake supply whatever production is needed to balance production against consumption.

Sodium carbonate and the products of the chlor-alkali industry, chlorine and caustic soda, are interrelated because they are all produced from a common raw material—sodium chloride. Continued increase in the demand for chlorine periodically threatens an oversupply of caustic soda, as the two are coproducts of salt-brine electrolysis. Thus far the market for caustic soda has kept pace with production; however, the sodium carbonate market is a possible outlet for excess caustic soda if barriers of price and traditional usage can be overcome. Some of the newer plants are designed for using either caustic or soda ash (*11*). One direct result of the increased consumption of chlorine is that byproduct caustic soda is replacing that formerly produced by the reaction of sodium carbonate and calcium hydroxide, and a formerly important use of sodium carbonate has become one of minor importance.

ALTERNATE MATERIALS

Salt is so abundant and low in cost that few substances can be profitably substituted for it. In dust, ice and snow control on highways, the physical and chemical characteristics of calcium chloride, aluminum chloride and certain other substances may be equal or superior to those of salt. However, economic factors usually favor salt.

In an underground salt mine, coarse grades of salt have been used as aggregate in concrete. This is only feasible where the structure is protected from moisture. The resulting "salt-crete" made with saturated brine, cement, and graded rock salt develops 75 percent of the strength of ordinary concrete.

Although salt is essential to health, certain illnesses are attributed to excessive retention of sodium in the body fluids. In the treatment of such illnesses low-salt or salt-free diets may be prescribed in which various salts such as potassium chloride (KCl) and flavoring extracts are mixed and substituted for salt.

A mixture of sodium carbonate and sulfur is a practical but more costly substitute for sodium sulfate in the digestion of wood chips for paper pulp.

Caustic soda may be used instead of soda ash in extracting alumina from bauxite.

Magnesium may be substituted for sodium as a reducing agent in certain metallurgical operations such as the reduction of $TiCl_4$ to titanium.

There are several substitutes for liquid sodium in cooling atomic reactors. Water, both light and heavy, and gases, such as helium and carbon dioxide, may be substituted for sodium to remove the heat from certain types of nuclear reactors.

SECONDARY SOURCES AND RECOVERY

Secondary recovery generally is not a significant feature of these industries. However, sodium sulfate is being recovered from waste liquors by the paper and pulp industry. Recovery systems not only collect the salt for recycling but also help to control stream-pollution problems. Average makeup of sodium sulfate per ton of pulp has been reduced from 200–400 pounds to 175–200 pounds and further reductions are possible. Recovery systems usually employ Cottrell precipitators.

RESERVES

Sodium Chloride

Exclusive of naturally occurring brines such as the seas, salt lakes, and salt springs, salt as rock salt reserves in the United States are astronomical; they have been estimated at 60,000 billion tons. At 100 times the present consumption and at a 50-percent recovery, these reserves are sufficient for 100,000 years. Each year as prospecting and exploration by drilling to greater depths continues primarily for petroleum and natural gas, many beds or domes of salt are being discovered. It can therefore be assumed that the United States has adequate salt reserves and resources for the present and future expanding needs.

The rock salt resources of the United States occur in four major areas or deposits and many other smaller outlining deposits (*14*, *21*, *27*).

Presently, the most productive deposits are the Silurian salt beds of the Northeastern States, which are one of the great accumulations of salt in the world. These deposits, in the Salina formation or group which is of late Silurian age, have an estimated average thickness of 150 feet over an area of 100,000 square miles underlying parts of New York, Pennsylvania, West Virginia, Ohio, Michigan, and southwestern Ontario.

The Permian basin deposits underlie parts of Kansas, Colorado, Oklahoma, Texas, and New

Mexico. Salt, which occurs in strata of Permian age, underlies an area about 650 miles from north to south and 150 to 250 miles from east to west, or about 120,000 square miles. The thickness of the salt-bearing beds are variable, but over much of the basin they range from 0 to 600 feet.

Salt deposits commonly called the gulf coast embayment are said to underlie 180,000 square miles of southern Arkansas, Mississippi, Alabama, eastern and southen Texas, and Louisiana and continue southward beneath the Gulf of Mexico. In southern Arkansas and northern Louisiana, bedded salt has been found at great depth in drill holes. It is thought that these Louann salt beds of Jurassic age continue southward at a greater depth than has been reached in drilling and that they are the source of the salt forming the more than 300 known salt domes along the coast of Texas and Louisiana and in the interior of northern Texas, northern Louisiana, and southern Mississippi. These domes are massive, extending several thousand feet both horizontally and vertically, with the top in many cases extending to very near the surface; which allows for easy and low-cost extraction.

Recent drilling for oil and gas in the Williston basin has disclosed 11 salt beds at depths ranging from 4,000 to 12,000 feet below the surface and from 100 to 400 feet in thickness. The Williston basin is a large sedimentary, structural basin underlying most of North Dakota, eastern Montana, northern and central South Dakota, and part of southern Canada. The 11 beds contain an estimated total volume of 1,700 cubic miles of salt in that part of the Williston basin underlying North Dakota.

In addition to these four major deposits, small occurrences of salt are known to underlie parts of many other States, including eastern Utah and southwestern Colorado in the Paradox basin, eastern Arizona and western New Mexico in the Supai basin, central Utah in the Sevier Valley, southeastern Nevada in the Virgin Valley, southwest Wyoming, northwestern Nebraska, and southern Florida.

Sodium Carbonate

Sodium carbonate requirements are supplied by manufactured soda ash from the ammonia-soda ash process and from natural sources of trona mined from the Green River formation in Wyoming and from brines from Searles and Owens Lakes in California. Each year a greater portion of the sodium carbonate production is being produced from natural sources; 9 percent in 1953 compared with 19 percent in 1963.

The area of the trona bed currently being mined in Wyoming is about 60 square miles, the thickness ranges from 7 to 16 feet, and the depth averages 1,500 feet. It is estimated that more than 650 million tons of soda ash can be produced from this area (*14*), which would supply the total U.S. needs for soda ash for more than 100 years at the present consumption rate. In addition, the reserves of brine in California from which sodium carbonate, sodium sulfate, and other minerals are recovered are large.

Sodium Sulfate

The supply of natural sulfate in Western United States is virtually inexhaustible with a reserve of hundreds of millions of tons (*36*). In addition to the presently mined natural sodium sulfate deposits of California, Texas, and Wyoming, deposits occur in Arizona, Nevada, New Mexico, North Dakota, Oregon, Utah, and Washington (*2*, *45*, *46*). Large deposits of sodium sulfate worked in Saskatchewan, Canada, are estimated to contain 200 million tons of glaubers salt (*24*). Large quantities of natural sodium sulfate occur at Lodosa in the Ebro Valley in Spain.

In addition to the byproduct and coproduct source and to the tremendous reserves of natural salts, there are plentiful reserves of the raw materials, salt, limestone, and sulfur from which to manufacture sodium sulfate and carbonate to meet all future demands for these compounds.

CONSERVATION PRACTICES

The primary sources of salt, sodium carbonate, and sodium sulfate are so ample that conservation is seldom considered. Although oil-well brines have a high salt content, they are more generally a disposal problem than a source of salt. Some sodium sulfate is recovered from some pulp and paper plant waste, previously discharged in streams, and is reused in these plants.

Large-scale conversion of saline water to fresh water must be considered as a factor that may influence future salt production. However, salt is generally a low-cost material and the bulk of it must be produced near the point of use to minimize the transportation cost. In addition, in present-day conversion plants only about one-half or less of the water is removed as fresh water from the sea water, whereas about nine-tenths of the water must be evaporated from the brine before salt will crystallize. If the salt is to be recovered from the brine by solar evaporation, the saline water conversion plant must be favorably located so that certain factors are present, as described in the "production

methods" section, for an economically successful solar plant operation.

SOURCES OF STATISTICAL INFORMATION

An annual survey of the salt producers in the United States and Puerto Rico is conducted by the Bureau of Mines. Coverage of the industry is virtually 100 percent; the respondents report tonnage and value of the various types of salt sold or used. They also record information on the markets for which the salt is destined and the State to which shipments are made. The information is tabulated and assembled in tables published in Mineral Industry Surveys and the Minerals Yearbook.

Figures on imports and exports of salt are obtained from the Bureau of the Census and published in the Minerals Yearbook.

All producers of natural sodium sulfate and sodium carbonate are canvassed monthly by the Bureau of Mines, and the production information is included in the Bureau of the Census Current Industrial Reports Series. These producers are also canvassed annually, and the commodity data are published in Minerals Yearbook.

Figures on the annual production of sodium metal are published by the Bureau of the Census.

PRODUCTION, CONSUMPTION, AND TRADE

Salt

U.S. salt production has shown steady growth since 1946 and more than doubled between 1946 and 1963. During this period, world production nearly tripled. Production of salt in the United States for 1959–63 and the average for the preceding 5 years is shown in table 1. U.S. salt production of 30.6 million tons was about 29 percent of the world production of 105 million tons in 1963.

TABLE 1.—*Salient statistics of the salt industry*

[Thousand short tons and thousand dollars]

	1954–58 (average)	1959	1960	1961	1962	1963
United States:						
Sold or used by producers:						
Evaporated:						
Bulk:						
Open pans or grainers	381	326	317	315	316	309
Vacuum pans	2,090	2,088	2,109	2,183	2,305	2,334
Solar	1,146	1,275	1,346	1,532	1,656	1,766
Pressed block	282	288	330	357	366	365
Total	3,899	3,977	4,102	4,387	4,643	4,774
Value [1]	$53,822	$67,925	$69,718	$70,467	$75,075	$77,066
Rock:						
Bulk	5,242	6,105	6,406	6,376	7,665	8,285
Pressed block	55	55	60	63	61	60
Total	5,297	6,160	6,466	6,439	7,726	8,345
Value	$33,969	$41,119	$44,983	$42,950	$46,874	$51,648
In brine: (sold or used as such)	13,473	15,023	14,911	14,881	16,438	17,525
Value	$43,326	$46,795	$46,439	$46,806	$52,892	$55,921
Grand total	22,669	25,160	25,479	25,707	28,807	30,644
Value	$131,117	$155,839	$161,140	$160,223	$174,841	$184,635
Imports for consumption	395	1,025	1,057	1,050	1,374	1,371
Value	$2,257	$5,438	$4,484	$3,755	$5,097	$5,074
Exports	376	424	420	642	671	781
Value	$2,687	$2,660	$2,548	$3,876	$3,638	$4,140
Apparent consumption	22,688	25,761	26,116	26,115	29,510	31,234
World: Production	74,900	87,900	93,600	93,400	100,700	104,900

[1] Values are f.o.b. mine or refinery and do not include cost of cooperate or containers.

In the United States about two-thirds of all salt is produced as artificial brine by drilling into deposits of salt and injecting water. Most brine is used for chemical purposes, and the wells are owned and operated by the producing companies. Salt from these "captive" wells is usually transformed or incorporated into another product and is seldom sold as salt.

Consumption of salt by various uses or consumer groups for 1959–63 and the average for the preceding 5 years is shown in table 2. Direct and indirect uses of salt in the United States for the specific years of 1953, 1958, and 1963 are shown in table 3 to point out the changes in the uses. Direct use as a freezing point depressant, primarily for deicing and melting snow on roads, has increased substantially as has the indirect use for manufacturing chlorine-caustic; however, the

indirect use for producing soda ash has decreased.

Imports and exports of salt, as shown in tables 4 and 5, are minor factors in the salt economy; imports were 4.4 percent of the apparent consumption and exports were about one-half of the imports in 1963. Nearly three-quarters of the 1963 U.S. salt imports came from the bordering countries of Canada and Mexico, but substantial quantities also came from the Bahamas, Spain, Tunisia, and Egypt. Of the U.S. salt exported in 1963, nearly three-quarters was shipped to Japan and about one-fifth went to Canada.

A new tariff law referred to as the Tariff Classification Act became effective on August 31, 1963. The duty on salt imported into the United States in brine is 10 percent ad valorem, in bulk $0.017 per 100 pounds, and other (packaged) $0.035 per 100 pounds.

TABLE 2.—*Salt sold or used by producers in the United States, by classes and consumers or uses*

[Thousand short tons]

Classes and consumer or uses	1954–58 (average)	1959	1960	1961	1962	1963
Chlorine	7,795	8,994	9,146	9,971	10,860	11,985
Soda ash	7,059	7,065	6,534	5,740	6,480	6,513
Textile and dyeing	199	219	195	199	215	260
Soap (including detergents)	42	37	36	36	133	35
All other chemicals	1,001	1,314	1,308	1,350	1,400	1,418
Meatpackers, tanners, and casing manufacturers	918	800	772	772	752	747
Fishing	36	33	29	31	24	26
Dairy	70	60	60	91	74	63
Canning	207	209	219	245	247	239
Baking	95	124	123	109	116	115
Flour processors (including cereal)	48	59	63	49	54	68
Other food processing	130	85	83	97	110	138
Ice manufacturers and cold storage companies	94	60	56	60	49	38
Feed dealers	764	902	946	975	1,037	1,030
Feed mixers	307	289	294	333	378	383
Metals	147	153	114	128	120	128
Ceramics (including glass)	17	14	12	14	20	15
Rubber	128	116	130	118	114	107
Oil	123	113	146	137	152	169
Paper and pulp	125	142	137	131	112	135
Water-softener manufacturers and service companies	396	352	396	423	442	507
Grocery stores	712	748	795	787	820	862
Railroads	89	62	53	42	54	51
Bus and transit companies	33	37	34	51	74	33
States, counties, and other political subdivisions (except Federal)	1,461	2,022	2,364	2,266	3,241	3,909
U.S. Government	40	36	37	60	140	665
Miscellaneous	634	1,115	1,397	1,492	1,589	1,005
Total	22,670	25,160	25,479	25,707	28,807	30,644

TABLE 3.—*Direct and indirect uses of salt in the United States*

Use	1953		1958		1963	
	Quantity (thousand short tons)	Percent of total	Quantity (thousand short tons)	Percent of total	Quantity (thousand short tons)	Percent of total
Direct uses:						
Nutrient or flavor	2,104	10	2,347	11	2,898	10
Preservative	1,041	5	833	4	773	3
Freezing point depressant [1]	976	5	1,912	9	4,696	15
Metallurgical processing	124	1	127	(2)	128	(2)
Miscellaneous processing	1,940	9	1,689	8	2,198	7
Total	6,185	30	6,908	32	10,693	35
Indirect uses for chemical manufacturing:						
Chlorine-caustic soda	6,065	29	7,729	35	11,985	39
Soda ash	7,846	38	6,180	28	6,513	21
Other chemical	693	3	1,095	5	1,453	5
Total	14,604	70	15,004	68	19,951	65
Grand total	20,789	100	21,912	100	30,644	100

[1] Includes use as deicer and stabilizer for roads.
[2] Less than 1 percent.

TABLE 4.—*Salt imported for consumption in the United States, by countries*

[Thousand short tons]

Country	1961	1962	1963
North America:			
Bahamas	190	203	213
Canada	382	678	645
Dominican Republic	65	29	
Jamaica	7	11	10
Mexico	387	407	353
Other [1]			
Total	1,031	1,329	1,221
Europe:			
Italy			
Spain	19	45	116
Other [2]		(3)	(3)
Total	19	45	116
Asia: Japan		(3)	
Africa [4]			34
Grand total	1,050	1,374	1,371

[1] Includes Leeward and Windward Islands, Trinidad and Tobago.
[2] Includes United Kingdom and West Germany in 1960 and United Kingdom only in 1962 and 1963.
[3] Less than 1,000 tons.
[4] Tunisia 26,000 tons and United Arab Republic (Egypt) 8,000 tons.

Source: Bureau of the Census.

TABLE 5.—*Salt exported from the United States, by countries*

[Thousand short tons]

Country	1961	1962	1963
North America:			
Canada	96	120	152
Mexico	3	8	4
Other	6	4	13
Total	105	132	169
South America	3	5	8
Europe	6	11	12
Asia:			
Japan	516	506	563
Other	3	4	9
Total	519	510	572
Africa	5	6	12
Oceania	3	7	8
Grand total	642	671	781

Source: Bureau of the Census.

Sodium Carbonate and Sulfate

Domestic production figures for sodium carbonate and sodium sulfate, natural and manufactured, are shown in tables 6 and 7.

Although Solvay soda plants continue to produce the bulk of the soda ash consumed in the United States, an increasing proportion, 13 percent in 1958 and 19 percent in 1963, is derived from natural sources.

Soda ash is consumed chiefly by the glass and chemicals industries. In 1962, 44 percent of the output was used in producing glass, 26 percent in chemicals, 9 percent in pulp and paper, 5 percent in soap and detergents, 4 percent each in aluminum and for water treatment, and 8 percent for miscellaneous purposes.

Imports of sodium carbonate usually are negligible. U.S. exports in 1963 were 3 percent of the total sodium carbonate production and were higher than they have been since 1956.

The duty on sodium carbonate, calcined (soda ash) or hydrated and sesquicarbonate is $0.0025 per pound. For crude sodium sulfate (salt cake) the duty is free, anhydrous $0.50 per ton, and crystallized (glaubers salt) $1 per ton.

Natural sources provided 36 percent of the sodium sulfate produced in the United States in 1963. The remainder was recovered as byproducts of chemical processes, which produced rayon, cellophane, hydrochloric acid, sodium bichromate, boric acid, phenols, and miscellaneous chemicals.

The kraft paper industry consumed an estimated 70 percent of the total U.S. sodium sulfate production. It is also used in making glass, ceramic glazers, detergents, stock feeds, dyes, textiles, medicines, and various chemicals.

U.S. imports for consumption of sodium sulfate in 1963, 13 percent of the total U.S. production of manufactured and natural sodium sulfate, were the lowest since 1959. More than 52 percent came from Belgium-Luxembourg, and 42 percent from Canada. The remainder was

TABLE 6.—*Manufactured sodium carbonate produced and natural sodium carbonates sold or used by producers in the United States*

Year	Manufactured soda ash (ammonia-soda process) [1] [2] (thousand short tons)	Natural sodium carbonates [3]			Total production, manufactured and natural sodium carbonate (thousand short tons)
		Thousand short tons	Percent of total production	Value (thousand dollars)	
1954–58 (average)	4,718	615	11.5	$16,152	5,333
1959	4,904	735	13.0	19,078	5,639
1960	4,558	809	15.1	20,865	5,367
1961	4,516	806	15.1	20,444	5,322
1962	4,607	978	17.5	24,330	5,585
1963	4,682	1,119	19.3	27,616	5,801

[1] Bureau of the Census. [2] Includes quantities used to manufacture caustic soda, sodium bicarbonate, and finished light and dense soda ash.
[3] Soda ash and trona (sesquicarbonate).

TABLE 7.—*Sodium sulfate produced and sold or used by producers in the United States*

Year	Production [1] (thousand short tons)					Sold or used by producers (natural only)		
	Salt cake (crude)	Glaubers salt (100 percent $Na_2SO_4 \cdot 10H_2O$) [2]	Glaubers salt (calculated 100 percent Na_2SO_4)	Anhydrous refined (100 percent Na_2SO_4)	Total manufactured and natural	Thousand short tons [3]	Percent of total manufactured and natural	Value (thousand dollars)
1954–58 (average)	702	135	60	258	1,020	309	30	$5,793
1959	734	99	44	308	1,086	403	37	7,689
1960	738	72	32	303	1,073	450	42	8,706
1961	780	64	28	327	1,135	466	41	9,296
1962	[3] 826	(4)	(4)	368	1,194	458	38	9,092
1963	[3] 837	(4)	(4)	396	1,233	435	36	8,392

[1] Bureau of the Census.
[2] Excluded from total manufactured and natural.
[3] Includes glaubers salt converted to 100-percent Na_2SO_4 basis.
[4] Included with salt cake (crude).

from the United Kingdom, West Germany, and the Netherlands. Exports, about 4 percent of the U.S. total output of sodium sulfate, went primarily to Mexico and Canada.

Sodium

Domestic output of metallic sodium, as shown in table 8, is used chiefly in producing tetraethyl and tetramethyl lead, fuels additive to increase their antiknock characteristics. Other important uses include metal descaling, ore reduction, and the manufacture of sodium peroxide, hydride amide, cyanide, borohydride, and other chemicals.

TABLE 8.—*Sodium metal production in the United States*

Year:	*Short tons*
1954–58 (average)	124,176
1959	112,019
1960	113,428
1961	109,100
1962	119,084
1963	125,566

STRATEGIC CONSIDERATIONS

The United States is self-sufficient in salt, sodium carbonate, and sodium sulfate, not only because of ample natural reserves but also because of abundant raw materials and capacity for producing manufactured varieties. The United States has an estimated 85 percent of the world production of metallic sodium.

PRICES AND COSTS

Prices of rock and table salt quoted in Oil, Paint and Drug Reporter have remained steady since February 1958: $1.09 per 100 pounds for rock salt in paper bags and in carlots, f.o.b. New York, and $1.34 per 100 pounds for vacuum, common fine, table salt on the same basis. The average value of rock salt (bulk salt and pressed block) at the mine as reported to the Bureau of Mines has decreased from an average of $6.87 per ton in 1958 to $6.19 per ton in 1963. Similarly, the average value of evaporated salt (open pans or grainers, vacuum pans, and solar salt and pressed block) decreased from $16.58 per ton in 1958 to $16.14 in 1963. Salt brine is seldom sold because it is usually produced and used as such by the same company. For such captive wells, the values are usually arbitrarily assigned. The average value of the salt in brines as reported by producers in 1963 was $3.19 per ton, compared to $3.30 in 1958.

Packaged-salt prices have not advanced in proportion to other commodities; a 26-ounce box of salt costing 10 cents in 1925 cost 11 cents in 1963.

Salt is a cheap, bulky commodity, and transportation charges are an important part of the cost. For this reason salt is sold largely in marketing areas near the producing areas.

Other factors besides transportation costs affect the price of salt. Salt is sold on a delivered basis; the grade of the salt, whether or not it is bagged, the size of the shipment, and the distance to market may be reflected in the price.

Salt is consumed in every part of the Nation for many different purposes. To insure profits, the industry depends on high sales volume and low unit costs. Although salt deposits are more than ample and reasonably well scattered in the Nation as a whole, they are not close to all centers of population and industry. In some instances the cost of transportation from the mine or producing area to the consumer is a major part of the delivered price.

Salt production requires a large capital investment in mining, refining, and packaging equipment; for solar salt a large investment in land is added. Nearly 90 percent of the total salt production sells for less than $10 per ton, which means that many tons must be sold to equal the fixed charges on the plant investment.

Because the quality of salt from one producer usually is substantially the same as that from any other, the only way to meet competition is through price. Transportation costs being an

important factor in the price, the producer with favorable freight rates between producing area and market has an advantage. This fact and the need to maintain a large sales volume in order to meet high fixed costs combine to make the salt industry highly competitive.

Prices quoted for sodium carbonate, sodium sulfate, and metallic sodium by Oil, Paint and Drug Reporter in 1963 were unchanged from those quoted at the close of 1958. Dense soda ash (58 percent Na_2O) in carlots and at the works sold for $1.60 per 100 pounds in bulk and $1.90 in paper bags. On the same basis light soda ash was quoted at $1.55 and $1.85, respectively.

Domestic salt cake (100 percent Na_2SO_4) in bulk and at the works sold for $28 per ton. Sodium sulfate of technical detergent and rayon grade sold for $34 per ton in bulk at works and for $38 per ton in bags and in carlots. Technical anhydrous sodium sulfate was priced at $56 per ton in bags and carlots.

Sodium metal in bulk, in tank cars, at works, was quoted at $0.17 per pound. Fused metallic sodium in lots of 18,000 pounds or more at the works was $0.195 per pound and in 5- or 12-pound bricks on the same basis was quoted at $0.21 per pound.

TAXES

For tax purposes a depletion allowance of 10 percent is allowed by the Internal Revenue Code for both foreign and domestic deposits of salt. Sodium sulfate and sodium carbonate are permitted a depletion allowance of 15 percent for both domestic and foreign deposits.

TRANSPORTATION

Salt is transported mainly by rail, and whether or not a producer can sell profitably in a given area depends in large measure on the freight rates. Some salt is moved by barge and some by ship. Over short distances salt brine is sometimes moved by pipeline. A new service to the chemical industries of the Beaumont-Port Arthur area was started in 1959 by a Texas concern, which began to supply brine by pipeline to customers.

Transportation of sodium sulfate and sodium carbonate is largely by rail. In some areas, particularly in the South, sodium carbonate is moved by barge. There are also shipments by sea. Bulk sodium metal is transported by tank cars specially equipped with heating pipes to melt the metal so that it can be pumped in and out of the cars.

Natural soda ash sources are found only in the western half of the United States and ammonia soda producers have always held a geographical advantage in being nearer to eastern markets where 80 percent of the soda ash is consumed. This advantage has been offset in part by reduced freight rates for soda ash and development of a high-capacity, 95-ton freight car, enabling western producers of natural soda ash to compete in many areas previously unavailable to them. The grade of the finished product, whether made from salt or natural soda compounds, is virtually the same (*25*). A substantial reduction in transcontinental freight rates was put into effect in October 1962, making western salt cake more competitive with that of eastern in the southeastern paper pulp area. Other freight rates were adjusted to enable eastern producers to maintain their share of markets (*26*).

RESEARCH

Research on production methods, uses, and products is carried on to a great extent by individual companies. Some of the major producers of salt and sodium compounds maintain large research laboratories in the search for new materials, methods, uses, and products and the improvement of product quality. Many improvements in mining and milling methods have been developed by the salt industry in the last 5 years. Examples of some of the technologic developments in mining include improvements in salt solution mining methods (hydraulic-fracturing techniques applied to salt mining), in bench mining methods in salt domes, and in blasting methods (application of ammonium-nitrate explosive). Milling developments include double-effect evaporation (recrystallizing) to purify salt, compaction of fines (as ribbons that are crushed and sized) using rollers to utilize surplus fines, and thermoadhesive methods of separating salt from waste.

Improved and more efficient chlorine caustic cells have resulted from research programs of industry.

Sodium metal and chlorine gas, primary products of the electrolysis of salt, have found wide application in many fields as a result of research programs. Particularly in the field of metallurgy, both sodium and chlorine have become increasingly important in the preparation of metals not amenable to conventional reduction procedures.

Producers of both soda ash and salt cake constantly seek new and improved methods for crystallizing the salts in their various forms from solution. For example, a process developed by a major producer depends upon refrigeration rather than evaporation for crystallizing sodium sulfate (*10*).

The Bureau of Mines has examined deposits of natural sodium sulfate in North Dakota, Utah, and Wyoming (*5*, *26*). A report was published (*42*) on a method of analyzing demand for mineral commodities, using a case study of salt. Data on methods and costs of shaft sinking and drifting in salt were reported (*16*).

A satisfactory solution mining technique for trona deposits has been the goal of a research program conducted by a large producer of soda ash. This company also maintains a mining-research team to study problems associated with mining trona. Use of a continuous miner is being studied.

Much research effort has been expended on sodium metal, both in perfecting its production and in finding new applications and handling procedures. Present production research includes reduction of sodium carbonate with carbon at a high temperature and condensing the resulting sodium vapor. Improvements in electrolytic techniques have also come about through research.

OUTLOOK

SODIUM CHLORIDE

The United States should continue to be the largest producer and consumer of salt; per capita salt consumption in the United States increased from 261 pounds in 1953 to 330 pounds in 1963. This ever-increasing per capita consumption coupled with a growing population and ample reserves are indications for an outlook of continued rise in the production and use of salt. Increased consumption will result as it has in the past, from new and expanded uses for salt and from a public demand for more and finer products requiring salt for processing or manufacturing them.

Salt will continue as a mainstay of the chemical industry because salt is one of the basic raw materials used for producing chemicals. Two-thirds of all salt sold or used in the United States in 1963, 20 million tons of the 31 million total, was consumed to produce chlorine, caustic soda, soda ash, salt cake, hydrochloric acid, and other chemicals. The remaining one-third of the total had hundreds of direct uses required by individuals as a nutrient or flavor, food preservative, freezing point depressant, and for processing in miscellaneous industries such as metals, ceramics, rubber, oil, paper and pulp, and water treatment.

Salt, through its importance to the chemical industry and through its widespread direct and indirect uses, will continue to reach into every segment of the industrial economy. This is evidenced by the fact that salt consumption has always correlated closely with the gross national product (GNP). Based on this and an anticipated annual growth rate of 3.8 percent (compounded) in the GNP, salt consumption in the United States is expected to increase from 31 million tons in 1963 to 60 million tons by 1980 and to 125 million tons by the year 2000. The average annual rate of growth of salt consumption during the last decade, 1953–63, has been 4.0 percent, exceeding that of GNP. If this trend continues, salt consumption by 2000 may quintuple that of 1963.

Changes in the consumption patterns for salt reflect the changing technology and demands by individuals and industries. Before 1955 Solvay soda production was the chief consumer of salt; in this process the chlorine content is largely wasted. However, the demand for chlorine by the chemical industry has been increasing steadily and has caused the chlorine-caustic industry to expand so that since 1955 the chlorine-caustic industry surpassed the soda-ash industry as a consumer of salt. In 1953, 29 percent of the salt sold or used by producers in the United States was consumed in the production of chlorine-caustic soda, compared with 35 percent in 1958, and 39 percent in 1963. This trend of an increasing amount of the salt output being used each year for chlorine production accompanied by a decreasing amount consumed in manufacturing soda ash is expected to continue.

Other growing uses for salt that are expected to continue to increase are those for road stabilization and highway snow and ice removal. These uses constituted an estimated 5 percent of the total salt production in 1953, compared with 8 percent in 1958 and 13 percent in 1963. Although it now represents less than 2 percent of the total salt output, more salt is being used each year in the regeneration of water softeners using the ion-exchange principle.

SODIUM CARBONATE

The total U.S. production of sodium carbonate, including both manufactured and natural soda ash production, should continue its growth at about the same rate it has in past years. The past growth compares closely with the anticipated growth rate of GNP (3.8 percent) for the next 10 to 20 years. On this basis, total soda ash production should reach 11 million short tons by 1980 and 23 million short tons by the year 2000.

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The recent growth in the soda ash industry has been largely from natural soda ash rather than ammonia soda production. The high capitalization required for new ammonia soda plants compared with natural soda ash production installations is the reason for the stalemate in new ammonia soda plant construction and increased interest in natural soda ash output. As a result, natural soda producers have increased plant capacities and other chemical companies have opened or announced plans for opening new mining and processing plants or are conducting exploration and development programs on vast underground trona deposits in Wyoming. Natural sodium carbonate output supplied 19 percent of the total manufactured and natural soda ash production in 1963, compared with 8 percent in 1953. This trend of a larger share of the market for sodium carbonate being supplied by natural soda ash is expected to continue.

Although not foreseen in the immediate future, growth in chlorine consumption under present technology eventually may cause an overproduction of the coproduct, caustic soda, which is a substitute for soda ash, and thus depress the demand for soda ash. However, new uses and substituting it for other chemicals has absorbed the extra production of caustic soda.

Another factor that may effect the future output of soda ash is the increased use of liquid detergents resulting in greater use of potassium compounds at the expense of sodium compounds. Reduction in the freight rates for shipping soda ash from western producing areas to eastern users has made western natural soda ash production competitive with eastern manufactured soda ash. The shift from the use of glass to plastic containers for some commodities has reduced the demand for soda ash for the production of glass, the major consuming industry. The alumina industry, which formerly relied heavily on soda ash to digest alumina ores, has largely converted to the use of caustic soda. However, in many plants either caustic soda or soda ash may be used.

SODIUM SULFATE

Production of sodium sulfate is expected to show continued growth, subject to severe fluctuations, because two-thirds of the total production of manufactured and natural output is recovered as a byproduct of chemical processes, which produced rayon, cellophane, hydrochloric acid, sodium bichromate, boric acid, phenols, and miscellaneous chemicals. The trend of a greater share of the total being supplied by natural sodium sulfate production is expected to continue; in 1953 natural represented 24 percent of the total compared with 36 percent in 1963.

The trend toward recovery of hydrochloric acid as a byproduct of certain chlorination reactions should diminish the importance of the Mannheim furnace for producing both sodium sulfate and hydrochloric acid. Widespread use of other fibers such as nylon in place of rayon reduced the production of byproduct salt cake from rayon manufacturers. Trends toward lower consumption of sulfate per ton of pulp and recovery and reuse of sulfate in the digestion of pulp, primarily affected to reduce stream pollution, slackened the demand for sodium sulfate for this use. Cellophane manufacturers could produce a substantial quantity of byproduct salt cake, but only one had installed recovery equipment.

Despite these fluctuations in supply of byproduct salt cake, several Texas and California natural sodium sulfate producers have expanded their plant capacities in late years. Natural sodium sulfate producers, which have ample reserves and production capacities, are expected to fill any demand gaps that may appear in industries normally supplied by byproduct salt cake.

SODIUM METAL

The supply and demand outlook for sodium metal is for continued minor fluctuations of production. The chief use of metallic sodium, in producing tetraethyl lead (TEL) and tetramethyl lead (TML)—two compounds added to motor fuels to increase their antiknock rating—will be affected by the production and use of economy cars that do not require high-test fuels. An increasing use of jet aircraft, which use no antiknock fuel additives, may adversely affect the demand for antiknock fuel. The introduction of gas turbines or other propulsion devices in place of internal combustion engines may also curtail the demand for sodium to produce tetraethyl lead. However, increased and expanded use of sodium metal for other and new uses is expected to take up any slack in demand.

Although the present consumption of sodium metal in nuclear reactors is negligible, large-scale developments of power by sodium-cooled reactors would require sizable quantities of very pure sodium at the beginning and modest quantities for makeup.

PROBLEMS

The problems of the salt industry are chiefly those of maintaining production and transportation costs low enough to continue to produce salt as a high-volume low-unit-cost commodity. To do this, improvements in mining, producing, processing, handling, and marketing methods and techniques are constantly needed to reduce labor costs or to compensate for increased labor and material costs.

One of the major problems of the salt industry is the high capital investment necessary for a plant to produce salt on an economical basis. The corrosive nature of salt and salt solutions causes rapid deterioration of the plant and equipment and contamination of the product. This is reduced by wider use of more expensive metals such as stainless steel and Monel. A second reason for the required excessive plant investment is the large-volume output or high minimum capacity necessary for an operation to produce salt at a low-unit cost.

Arresting the external corrosion of well casing in brine wells is a continuing problem. When used on highways for dust and ice control, salt causes deterioration of vehicles and road surfaces.

The salt industry also is faced with the problem of continually improving methods of upgrading the quality of rock and evaporated salt by removing or discarding the impurities at a low cost to meet industry or consumer demands. This is being done and must continue to be done through advances in the beneficiation methods such as the recently developed and employed recrystallizing, electronic scanning, thermoadhesive, and other methods of purifying salt. Caking of salt during storage causes a problem in handling the material with mechanized equipment.

The salt industry must consider the problem of how it will participate and be affected in certain areas, particularly those with a deficient supply of fresh water, if desalting of sea water becomes a major commercial reality and if it is feasible to utilize the effluent or brines from the saline water conversion plants for producing salt and other chemicals.

Many of the problems of producing and marketing sodium carbonate are similar to those for sodium chloride. High capital investment required for constructing new ammonia-soda plants has been a restrictive factor in developing new or for increasing plant capacity for manufacturing sodium carbonate. This has resulted in the increased development and use of the natural soda ash deposits of the Western United States. As with salt, transportation costs for soda ash are an important part of the delivered price of the commodity. Therefore, the problem of transporting the natural soda ash produced in the West to the consumers and major markets at a low cost must be considered.

Other problems of mining and processing sodium carbonate from natural sources are: (1) floor heaving, which interferes with efficient underground mining in one operation; (2) lack of an efficient solution mining method for underground trona deposits; and (3) lack of simple methods for controlling the crystallization of desired types of sodium compounds from solution. Lack of markets for byproduct calcium chloride produced at ammonia-soda plants contributes to the production costs of manufactured sodium carbonate.

The major problem in the sodium sulfate industry is that most of the market is supplied by byproduct material recovered from the production of other commodities and this supply fluctuates with the demand and production of other chemicals. The natural sodium sulfate producers are located in the Western United States and their production costs must be reduced if natural sodium sulfate is to compete with byproduct manufactured sodium sulfate because sodium sulfate must remain a low-unit-cost item and transportation costs from the West are relatively high. The industry also has technical problems relating to purifying, evaporating, and dehydrating byproduct sodium sulfate crystals from solution.

Problems of metallic sodium are largely technical and relate to the extreme reactivity of the metal, particularly in its liquid and vapor forms. The reactivity presents difficulties in handling, controlling reactions, and maintaining metallic sodium in the required state of purity.

Rapid technological changes in consuming industries pose problems for sodium compounds and sodium producers; markets are threatened and curtailed before new ones are created.

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STEEL

By Robert A. Whitman [1]

STEEL is primarily a refined alloy of iron and carbon, with carbon varying from 0.01 to 1.7 percent. When alloying elements are specified or intentionally added, in excess of certain limits established by the industry, to impart desired mechanical or chemical properties not otherwise obtainable with iron and carbon and nominal alloys, the product is classed as alloy steel.

The domestic steel industry, including rolling mills, is comprised of 218 companies with 422 plants, employing over one-half million people with an annual payroll of about $5 billion. Approximately 75 percent of this industry is located in the six States of Illinois, Indiana, Ohio, Michigan, Pennsylvania, and New York.

Annual capacity figures have not been reported by the steel industry since 1960. At that time capacity was reported at 148.6 million ingot tons. If capacity continues to expand at the rate of about 2 million tons annually, the capacity in 1965 should be about 160 million ingot tons.

The United States pours over one-fourth of the steel made in the world. Production in 1963 was nearly 109 million tons of steel ingots and steel for castings.

Eight and one-half million tons of ingot steel, 8 percent of the total output, came from basic oxygen converters in 1963. Open-hearth furnaces accounted for 81 percent, electric furnaces 10 percent, and Bessemer furnaces for about nine-tenths of a percent. Oxygen steelmaking was introduced into the United States in 1954. Five years later, in 1959, it accounted for 1.9 million tons or 2 percent. This increase in oxygen steelmaking in the last decade is indicative of the way that the steel industry has modernized during that period. For the last 15 years the steel industry has averaged $1 billion per year in capital expenditures. For the first 10 years most of this outlay was for increased production, but for the last 5 or 6 years the emphasis has shifted to increased productivity and newer products. Continuous casting machines and computers to calculate charges for blast furnaces, open-hearth and basic oxygen furnaces, and to control settings and speeds of rolling mills have been introduced.

The outlook for steel in the United States is for a continued gradual increase in consumption at a rate slightly higher than the population growth rate. A steel production figure of about 150 million tons is forecast for 1980.

The steel industry is spending about $100 million annually for research to improve both methods and products. Methods of reducing production costs, conserving raw materials, and improving existing products are being studied and developed by the industry. Fundamental research in the metallurgy, chemistry, physics, and interdisciplinary fields of these sciences as related to steelmaking is being conducted by private foundations and universities. The Bureau of Mines research program includes determination of physical and chemical properties of pelletized iron concentrates, causes of fuming in oxygen steelmaking, improvement of high-strength alloy steel ingots with rare-earth alloy additions, upgrading of submarginal iron ores by reduction-roasting with ferrous scrap, mechanisms of high-strength steel and cobalt hardening of stainless steel.

BACKGROUND

The exact date when steel was first made is not well established. However, archeological specimens estimated to have been made as long ago as 1000 B.C. indicate edges that were hardened by rapid quenching of the heated carburized steel. Another ancient steelmaking process, known as the crucible process, consisted of melting wrought iron in a clay crucible with

[1] Commodity specialist.

carbon to increase the carbon content of the iron. Steels produced by these processes include the Wootz steel of India, steel for the famous blades of Damascus, Syria, and the equally famous steels of Toledo, Spain.

During the Middle Ages both cementation and crucible methods appear to have been lost to civilization. The cementation process was revived in Belgium about 1600, and Benjamin Huntsman of England rediscovered the crucible process in 1742. The major breakthrough for the industry was the invention of the Bessemer process in 1856 in England. Although this process bears the name of Henry Bessemer, with a patent issued in 1856, Henry Kelley had experimented with the process as early as 1847 in the United States. The next great step in the creation of the steel industry was the invention of the open-hearth process by Karl Siemens in 1868.

The earliest instance of application of electricity to metallurgy is a patent granted on March 16, 1853, to the French chemist, Pichon. The first practical application of electric melting of steel was made by Sir William Siemens in England in 1879. Following the Siemens method came the Heroult electric-arc furnace in France in 1888–92. The next major advance in steelmaking occurred in 1952 with the installation of the first commercial plants to make steel by the Austrian Linz-Donawitz process or the oxygen steelmaking process at Linz and Donawitz, Austria.

The first recorded steel production in the United States was 917 tons of "blister" steel made in 1810 from bar iron. In 1832, the Girrard Brothers established a crucible-steel works in Cincinnati, Ohio. The steel industry, however, marks the beginning of commercial production of steel with the first commercial Bessemer production at Wyandotte, Mich., in September 1864. Thus in September 1964, the steel companies ushered in the second century of commercial steelmaking in the United States.

The prevalence of low-phosphorus iron ore in the United States prompted the development of the Bessemer process during the latter half of the 19th century, as opposed to the Thomas process, which is for high-phosphorus iron ore. Open-hearth steel production increased rapidly between 1900 and 1916, owing mainly to greater demand for quality steel and the inability of the Bessemer process to consume scrap. By 1925 open-hearth production made up 84 percent of total steel; by 1958 this figure had grown to 76 million tons, or 89 percent of total steel. Five years later in 1963, production of steel by the basic oxygen converter had risen to 8.5 million tons, and open-hearth production represented only 80 percent of the total steel produced. In 1964 production of steel by the basic oxygen converter had reached 15 million tons and open-hearth production had dropped to about 77 percent of total production.

Since World War II commercial production of steel by the crucible method has virtually stopped and production of steel by the Bessemer method has declined to less than 1 percent of the total. Electric production remains around 10 percent of total ingot production.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF INDUSTRY

The United States produces and consumes over one-fourth of the world's steel supply. In 1963, there were about 275 companies engaged in the manufacture of steel products. Of these there were 95 companies with 163 plants producing steel for ingots and castings. There were 16 companies that produced 1 million tons or more of ingot steel. The industry had an average annual payroll for over 787,000 employees of more than $5 billion. There were 244 blast furnaces which produced 72 million tons of pig iron. Total estimated investment of the steel industry was over $14 billion, and the net revenue from steel products sold approximated $14.5 billion (*5*).[2]

Over 75 percent of U.S. steel output is produced in the northern band of six States from New York to Illinois and including Michigan. There are heavy concentrations in the Pittsburgh-Youngstown area and in the Gary-South Chicago area. Table 1 gives steel production by States.

TABLE 1.—*Production of steel, by States*

[Thousand short tons]

State	1963
Pennsylvania	25,193
Ohio	18,777
Indiana	15,548
Illinois	9,214
Michigan	8,437
New York	5,386
Rhode Island, Connecticut, New Jersey, Delaware, Maryland	7,258
Alabama, Tennessee, Mississippi	3,851
Virginia, West Virginia, Georgia, Florida, North Carolina	3,677
Arizona, Colorado, Utah, Washington, Oregon, Hawaii	3,615
California	3,387
Minnesota, Missouri, Oklahoma, Texas	3,337
Kentucky	1,580
Total	109,261

Source: Annual Statistical Report, American Iron and Steel Institute.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

The term "pig iron" denotes a class of products made by reducing iron ore in the blast furnace. Included in the pig iron classification is silvery pig iron, an intermediate product between pig iron and ferrosilicon. These higher silicon-content irons can be made in either blast or electric furnaces. Chemical contents specified for grades of pig iron vary according to its intended end use. The following designates the various pig irons in the United States:

Designation		*Phosphorus content, percent*
LP	Low phosphorus	0.035 maximum
LPi	Intermediate low phosphorus	0.036 to 0.075
Bes	Bessemer	0.076 to 0.100
M	Malleable	0.101 to 0.300
B	Basic—Northern	0.400 maximum
Fl	Foundry—Northern, low phosphorus	0.300 to 0.500
Fh	Foundry—Northern high phosphorus	0.501 to 0.700
Fs	Foundry—Southern	0.700 to 0.900
Bs	Basic—Southern	0.700 to 0.900
S	Silvery	0.300 maximum

Silicon varies from 0.50 to 3.50 percent for the true pig irons and from 5 to 17 percent for silvery pig iron. Maximum limit for sulfur for most grades is 0.050 percent. Carbon content which cannot be controlled to close limits ranges from 3.50 to 4.40 percent and is generally not specified (*7*). Detailed chemical analyses according to grade designations are given in the reference cited. Pig iron may also be classified according to the raw materials used, for example, *charcoal pig*, *coke pig*, *hematite pig*, *titanium pig*, or *chromium-nickel pig*. In Europe, *Thomas pig iron*, which contains 1.7 to 2.2 percent phosphorus, is used for making steel in the Thomas (basic-lined) converter.

Iron and steel scrap is refuse ferrous materials, either alloyed or unalloyed, of which iron and steel are the principal components. It is classified as home and purchased scrap. *Home scrap* is produced at the iron and steel plant during the steelmaking and rerolling processes, which include such items as skulls, ingots, butts, crops, clippings, borings, and defective products discarded as well as old plant scrap. *Purchased scrap* includes scrap bought from other steel plants as well as scrap obtained from fabricators, railroads, other industrial plants and iron and steel scrap dealers. Purchased scrap is further classified as industrial and obsolescent. Industrial scrap is still further divided into prompt industrial scrap and other scrap. *Prompt industrial scrap* is the waste or byproduct of processes of fabricating iron and steel products. The *other industrial scrap* comprises products and parts of plants that have completed their service of life and have been discarded because of failure, obsolescence, or other reasons. Nonindustrial *obsolescent scrap*, sometimes referred to as *country scrap*, is the product of the same forces as the other industrial scrap. It comprises all kinds of equipment, usually worn out or outmoded (*8–12*).

Recirculated or home scrap accounted for about 64 percent of the scrap consumed in 1963 (*11*).

Up to 75 grades have been used by the trade in classifying iron and steel scrap. Many of the grades are similar in physical form and chemical composition. Because of this, the Bureau of Mines has condensed the many grades to 14 classifications, which cover all grades of iron and steel scrap (*4*, *12*).

Steel is primarily a refined alloy of iron and carbon containing up to 1.7 percent carbon. When alloy elements are intentionally added to steel to impart desired mechanical or chemical properties not otherwise obtainable with carbon alone, it is classed as an *alloy steel*. However, the ingredient that exerts the most influence on steel is carbon. High-grade razor steel contains about 1.25 percent of carbon; spring steel, 1 percent; steel rails, from 0.50 to 0.75 percent; and soft sheets may have as little as 0.04 percent of carbon. Steel low in carbon can be easily welded, but cannot be hardened appreciably; with carbon above 0.33 percent, welding is more difficult and can be done only by the use of borax or some other flux, or by the electric or thermit processes.

The hardness of steel may be altered by heat treatment to be one of the hardest metals known. For example, a fully hardened carbon steel with 1.20 percent carbon will have a hardness of Rockwell C 70 and an approximate tensile strength of 550,000 pounds per square inch. In tool steel, ingredients other than carbon are often used to influence its hardenability, wear resistance, and secondary hardness. These additives include tungsten, molybdenum, chromium, vanadium, and cobalt. Also, steel can be made into one of the strongest metals known through both the addition of alloying elements and heat treatment. By cold rolling and working at about 1,000° F strengths of over 350,000 pounds per square inch are possible (*1*, *16*, *19*).

Steels that derive their properties mainly from carbon, with no guaranteed or specified minimum alloy content, are classed as *carbon steels*. Some manufacturers class carbon steels according to the carbon content as follows: *High carbon*, over 0.55 percent; *medium carbon*, 0.25–0.55; and *low carbon* or *mild steel*, under 0.25. Others classify them according to the method of manufacture such as *acid open hearth*, *basic open hearth*, *electric*, or *Bessemer*. This classification may be extended further to

include the method of deoxidation used, for example, if oxygen is partly or completely removed by adding deoxidizers such as aluminum and silicon, the resulting steel is classed as *semi-killed* or *fully killed*, respectively. In *rimmed steel* part of the oxygen, nitrogen, and hydrogen is liberated from the steel during the rimming or effervescent action that occurs during solidification. The remainder stays in the steel and forms blowholes. In *mechanically capped steel*, all the gases are trapped in the steel by placing a heavy metal cap over the ingot mold during solidification of the ingot. Small quantities of aluminum are added to the latter two grades to control ingot structure.

Properties of all these steels may be modified by heat treatment to control microstructure and mechanical properties. For example, a coarse-grained carbon steel may be heated above the upper critical range 1,335° F and quenched in water to produce a hard steel with a greater tensile strength. Depth hardening is obtained by adding alloys that retard the rate of transformation of austenite to pearlite and ferrite. Flame hardening, case hardening, and nitriding are methods used when only the surface is to be hardened. Cold rolling also alters microstructure and mechanical properties (*13*, *19*).

The Bureau of Mines uses the American Iron and Steel Institute's specification for alloy steels which includes stainless and any other steel containing one or more of the following elements in the designated percentages: Manganese in excess of 1.65, silicon in excess of 0.60, and copper in excess of 0.60. The specification also includes steel containing the following elements in any amount specified or known to have been added to obtain a desired alloying effect: Aluminum, boron, chromium up to 3.99 percent, cobalt, columbium, molybdenum, nickel, titanium, tungsten, vanadium, zirconium, and other alloying elements (*4*).

Stainless and heat-resisting steels are generic terms. They do not designate any one steel but rather a whole family of steels whose common characteristic is a comparatively high chromium content. Stainless steel is basically an alloy of iron containing over 10 percent chromium. When chromium is added to iron in such quantities it imparts throughout the entire body of the metal remarkable resistance to corrosion and heat. Other elements may be added to the iron-chromium combination to obtain steels with special characteristics. The most important of these is nickel, which is used to produce 18–8-type steels; that is, 18 percent chromium, 8 percent nickel, balance iron. Other useful additions are columbium, manganese, molybdenum, nitrogen, selenium, silicon, sulfur, titanium, and zirconium, all of which result in modifications for special services or fabrications.

The standard stainless steel grades may be grouped according to microstructure, chemical composition, and response to heat treatment as follows:

1. *Ferritic.* Nonhardenable steels containing 11.5 to 27 percent chromium, with generally low-carbon contents (ranging from less than 0.08 to a maximum of 0.20 percent).
2. *Martensitic.* Hardenable (by quenching) steels containing 11.5 to 18 percent chromium, with carbon contents (ranging from less than 0.10 percent to 1.20 percent maximum).
3. *Austenitic.* Steels containing 16 to 26 percent chromium, 3.5 to 22 percent nickel, and 0.03 percent maximum to 0.25 percent maximum carbon, hardenable without quenching.

Nonstandard grades of alloys not included in these classifications that are still recognized as stainless steel, include special specifications of the standard grades and stainless steels with additions such as tungsten, vanadium, aluminum, copper, and phosphorus to convey special properties. These steels are used for certain applications. Two widely used heat-resistant steels not mentioned are AISI types 501 and 502, containing 4 to 6 percent chromium. These steels have good strength at elevated temperatures and are corrosion-resistant rather than stainless (*19*).

TECHNOLOGY

Steelmaking Materials

Steelmaking processes, using pig iron produced by the blast furnace, include the open hearth, Bessemer, and oxygen converters. The electric furnace utilizes nearly 100 percent scrap, however, on rare occasions up to 50 percent molten pig iron has been used. On a national basis the quantity of scrap consumed in all furnaces including iron foundries is approximately the same as pig iron.

Molten pig iron tapped from the blast furnace is usually transferred in ladles via railroad cars to refractory-lined hot metal mixers in the open hearth or oxygen steelmaking department, where it is kept hot until needed in steelmaking furnaces.

Although it is possible to reduce sulfur in the electric furnace, the removal of sulfur in the open hearth is somewhat uncertain, and when the open hearth fuels such as coke oven gas, fuel oil, tar, and the like contain any considerable amount of sulfur, the problem is aggravated.

To produce an acceptably low-sulfur steel, without increasing steel furnace refining time

sulfur must be removed from the iron when it is produced in the blast furnace.

Iron and steel scrap supplies approximately 50 percent of all metallics used in iron and steel furnaces in the United States. The essential characteristics governing the usefulness of scrap are its chemical composition and physical form. The use of rusted or corroded scrap may result in a metal yield as low as 60 percent. Scrap containing undesirable elements may affect refractories or cause other difficulties during melting and refining or cause the steel to be unfit for its intended use. The increase in residual copper, nickel, and tin in carbon steel is a major problem at many steel plants. Tin and copper cause minute surface tears in steel. Nickel and copper increase hardenability which adversely affects deep drawing properties.

In addition, the problem of scrap availability and price also must be considered.

The density of scrap is related directly to steel production. Furnace-scrap-charging boxes that give high scrap weights per cubic foot, using dense material, decrease furnace-charging time and make it possible to pull all the scrap in at one time (that is, it is unnecessary to melt down part of the scrap to make room for the complete charge). Heat losses during prolonged charging increase melting time. At some steel plants steel production rates have been increased by as much as 20 percent by using charging boxes with high-scrap weights per cubic foot (*3*).

There is a direct relationship between the composition of scrap and pig iron and the composition of the steel bath and slag. The elements present, except carbon, may be divided into four groups, according to their oxide stability and chemical reactions among the various elements present under oxidizing conditions in open-hearth furnaces. The removal of carbon depends on the degree of oxidation of the bath (*2*).

The four groups are:

Group 1.—Elements almost completely taken up by the slag: Silicon, aluminum, titanium, zirconium, boron, and vanadium.

Group 2.—Elements distributed between the slag and metal: Manganese, phosphorus, sulfur, and chromium.

Group 3.—Elements remaining almost completely in solution in the steel: Copper, nickel, tin, molybdenum, cobalt, tungsten, and probably arsenic and antimony.

Group 4.—Elements almost completely eliminated from slag and metal: Zinc, cadmium, and lead.

The elements in group 1 have no direct effect upon the composition of the metal, since they oxidize and are held in the slag. High-silicon scrap is undesirable, because the high-silica slag formed during the melting period attacks the furnace walls.

The effect of the elements listed in groups 2 and 3 depends on furnace practice and kind of steel being produced. Manganese is usually desirable, except in low-metalloid grades (0.10 percent maximum all elements except iron). Phosphorus usually is undesirable, but the maximum amount permissible is governed by the type of furnace practice, the grade of steel, and other components of the charge. For example, more phosphorus is usually permissible if the silicon content is low. Sulfur, arsenic, antimony, and tin are undesirable because they increase surface imperfections. Chromium, copper, nickel, molybdenum, cobalt, and tungsten may be desirable or undesirable, depending on the grade of steel being produced and the type of furnace used. For example, copper could be an asset for copper-bearing sheets for roofing but a detriment to type L tin plate having a 0.06 maximum copper specification (used for the certain corrosive foods).

The elements in group 4 have no effect on the slag or metal bath since they are eliminated during the melting and refining period, but they may be detrimental to the furnace and auxiliary equipment. Zinc oxide may clog tubes in waste-heat boilers. Excessive zinc in the charge also tends to shorten silica-brick life in roof and end zones of furnaces. Lead tends to melt and form channels between brick refractories, thus allowing molten steel to penetrate through the bottom.

The distribution of the foregoing four groups of elements in electric-furnace steelmaking is the same under basic oxidizing conditions but will vary under a reducing condition.

As there are only a few acid-lined furnaces in the United States, these are not discussed in this chapter.

The scrap portion of open-hearth charge ranges from 100 percent to zero, the balance being cold or molten pig iron. The average for hot-metal plants is 40 percent scrap, while cold-melt plants use 85 percent scrap. The national average for electric furnaces is 98 percent scrap and 2 percent pig iron. A Bessemer converter consumes very little scrap unless oxygen is used.

Additive Metals in Steel

Metals and other materials are added to steels to improve its physical properties. Some act as scavengers, counteracting the harmful effect of sulfur, removing gases, or decreasing inclusions. Others are added for their alloying effect or as both an alloy ingredient and scavenger.

Several theories and formulas are used by the iron and steel industry to determine the kinds and quantities of the alloys necessary to obtain desired mechanical properties.

A comparison of the effects of the chief alloying elements in steel is given as follows (*18*).

Strengthen ferrite

P—very strong
Si, Mn—strong
Ni, Cu, Cr, Mo, W—fairly strong
V—weak

Confer depth hardening

Mo, W, Mn, Cr—strong
Si—medium
Cu, Ni—weak
V—very weak

Restrain grain growth of austenite

Al—very strong
V, Ti, Zr—fairly strong
Mo—medium
Cr, Si—weak
Mn—very weak
Ni—practically no action

Form carbides

Ti, Nb, V—very strong
Cr, Mo, W—strong
Mn—fairly strong
P, Ni, Cu, Si—no carbides

Stabilize martensite and troostite on tempering

Mo, W—strong
V—fairly strong
Cr—weak
Mn—very weak
Others no appreciable stabilization

Decrease eutectoid content

Mn, Cr, V—considerably
Ni, Mo, W—somewhat
Si, Cu, Al—no appreciable effect

Some Specific Effects and Reason for Use

Al—Control of grain size; removes gases and impurities.
Cr—Small amounts improve hardening qualities; more than 10 percent prevents rust.
Co—Holds cutting edge at high temperatures; making magnet steels.
Cu—Over 0.75 percent, confers power of precipitation hardening.
Cu or Cu+P—Even in small amounts, confer improved resistance to atmospheric corrosion.
Pb and S—Improve machinability.
Mn—Small amounts remove gases from steel; 1 to 2 percent increases strength and toughness; 12 percent imparts great toughness and resistance to abrasion.
Mo—Minimizes temper brittleness; increases strength, ductility, and resistance to shock.
Mo, W—Confer high-temperature strength, especially in the presence of other carbide-forming elements.
Ni—Confers toughness without brittleness, and especially confers low-temperature impact toughness.
V—Increases strength, ductility, and resiliency.

The alloy steel may be used only as a surface skin. Thus stainless steel clad plate is made of an ordinary carbon steel to which there is uniformly and permanently bonded a veneer or cladding to one or both sides. This clad material may be substituted for a 100 percent stainless plate. It is less expensive and in most cases offers the same corrosion resistance as the steel or alloy for which it is substituted. Thickness of cladding generally ranges from 5 to 20 per cent of total thickness. In addition to cladding with stainless steel, high-purity nickel, aluminum, copper, titanium, and other metals may be used.

Steelmaking Processes

Steel may be made in an open-hearth furnace, a basic oxygen converter, an electric furnace, or a Bessemer furnace. The relative positions of the various steelmaking processes in the United States are given in figure 1 and table 14. Steel is the result of chemical reactions involving the refining of pig iron and scrap by oxidation and slag reactions whereby the quantities of carbon, silicon, and other removable, unwanted elements are lowered while the content of other elements is increased or decreased, depending on the kind of steel desired (*2*, *9*, *13*). Data on free energy of formation of oxides, sulfides, nitrides and carbides, and stability of oxides and sulfides for many of the metal and nonmetal compounds at steelmaking temperatures of 3,000° F are useful in predicting or determining the nature of the reactions that take place in steelmaking practices. For example, to predict the course of reactions between metals, slags, and gases (such as, reactions that occur in the control or removal of harmful impurities in steel), free energies of formation, heat capacities, and activities of the reacting substances are required.

The open-hearth furnace accounts for more than 75 percent of U.S. steel production. Modern open-hearth furnaces are of the reverberatory type, with a hearth in the shape of a large oval dish. At each end of the furnace are ports (where the fuel and air meet) connected to the refractory checkers-regenerators by flues. Through a system of valves and flues the checkers are connected either to the incoming air supply or the stack for waste gases. The utilization of heat from waste gases is possible by these valves, which automatically change the direction of the flow of air and gases about every 15 minutes to maintain a checker temperature of 1,800° to 2,200° F which is required for efficient operations.

Open-hearth furnaces are of two types—basic and acid. Basic furnaces are lined with magnesite or dolomite, while acid furnaces are lined with silica brick (*9*). In the basic furnace a lime basic slag facilitates the removal of silicon, phosphorus, and a limited quantity of sulfur. In the acid-lined open-hearth furnace, silica or acid slag does not eliminate phosphorus and sulfur, therefore, special types of pig iron are required for this type of furnace as well as carefully selected scrap. For this reason, practically all the open hearths in this country are of this basic type which facilitates the removal of these impurities.

Steel produced from each open-hearth furnace charge averages about 175 tons with furnace capacities per heat ranging up to 600 tons. The charge consists of pig iron (molten or cold), scrap, and limestone; and iron ore, if more than 50 percent molten pig iron is used. Molten metal is added after the scrap is partly melted.

TABLE 2.—*Growth of basic oxygen steelmaking capacity in the United States*

Company	Plant location	Number of furnaces	Output per heat (short tons)	Startup date	Annual capacity (thousand short tons)	
					Existing	Future additions
Acme Steel Co	Riverdale, Ill	2	75	1959	450	
Allegheny Ludlum Steel Corp	Brackenridge, Pa	1	20	1964	Experimental	
Do	Natrona, Pa	2	65	1966		Commercial
Armco Steel Corp	Ashland, Ky	2	150	1963	1,400	
Bethlehem Steel Co	Lackawanna, N.Y	2	250	1964		2,200
Do	Sparrows Point, Md	2	200	1966		1,800
Colorado Fuel & Iron Corp	Pueblo, Colo	2	100	1961	1,000	
Ford Motor Co	Dearborn, Mich	2	240	1964	2,000	
Inland Steel Co	East Chicago, Ind	2	230	1965		2,200
Jones & Laughlin Steel Corp	Aliquippa, Pa	2	85	1957	950	
Do	Cleveland, Ohio	2	230	1961	1,900	
Kaiser Steel Corp	Fontana, Calif	3	110	1958	1,440	
McLouth Steel Corp	Trenton, Mich	3	60	1954	2,000	
		2	105	1958		
		1	105	1960		
National Steel Corp.:						
Great Lakes Steel Corp	Ecorse, Mich	2	300	1962	2,500	
Weirton Steel Div	Weirton, W. Va	2	300	1966		2,500
Pittsburgh Steel Co	Monessen, Pa	2	150	1964	1,500	
Republic Steel Corp	Warren, Ohio	2	150	1965		1,500
Do	Gadsden, Ala	2	150	1965		1,500
Do	Cleveland, Ohio	2	220	1966		2,000
United States Steel Corp	Duquesne, Pa	2	150	1963	1,500	
Do	Gary, Ind	3	150	1965		3,000
Wheeling Steel Corp	Steubenville, Ohio	2	225	1964		2,000
Wisconsin Steel Div. of International Harvester Co.	South Chicago, Ill	2	120	1964		1,200
Total		51			[1] 16,640	19,900

[1] Does not include Kaldo plant at Sharon Steel Corp., Sharon, Pa.

Source: Kaiser Engineers Div., Kaiser Industries Corp., Oakland, Calif.

TABLE 3.—*World annual capacity for basic oxygen steelmaking*

[Thousand short tons]

Country	Existing	Future additions	Country	Existing	Future additions	Country	Existing	Future additions
Algeria	None	990	India	830	960	Tunisia	None	90
Australia	1,280	560	Italy	None	6,070	Turkey	None	520
Austria	1,980	None	Japan	18,890	5,490	United Kingdom	4,420	1,680
Belgium	1,770	4,910	Luxembourg	440	580	U.S.S.R	4,070	6,630
Brazil	1,050	680	Netherlands	2,500	None	Yugoslavia	None	660
Canada	3,100	None	Norway	500	None			
Finland	None	550	Peru	None	[2]	Total	53,110	33,230
France	3,370	None	Portugal	350	None	Total, United States	[3] 16,640	19,900
Germany, West	7,710	2,310	Spain	440	550			
Greece	300	[1]	Sweden	110	None	World total	69,750	53,130

[1] Two 40-ton furnaces are being added to Greece's present two 40-ton furnaces that have an annual capacity of 300,000 tons.
[2] No capacity given for two 30-ton furnaces being built in Peru.
[3] Does not include Kaldo plant of Sharon Steel Corp., Sharon, Pa.

Source: Kaiser Engineers Div., Kaiser Industries Corp., Oakland, Calif.

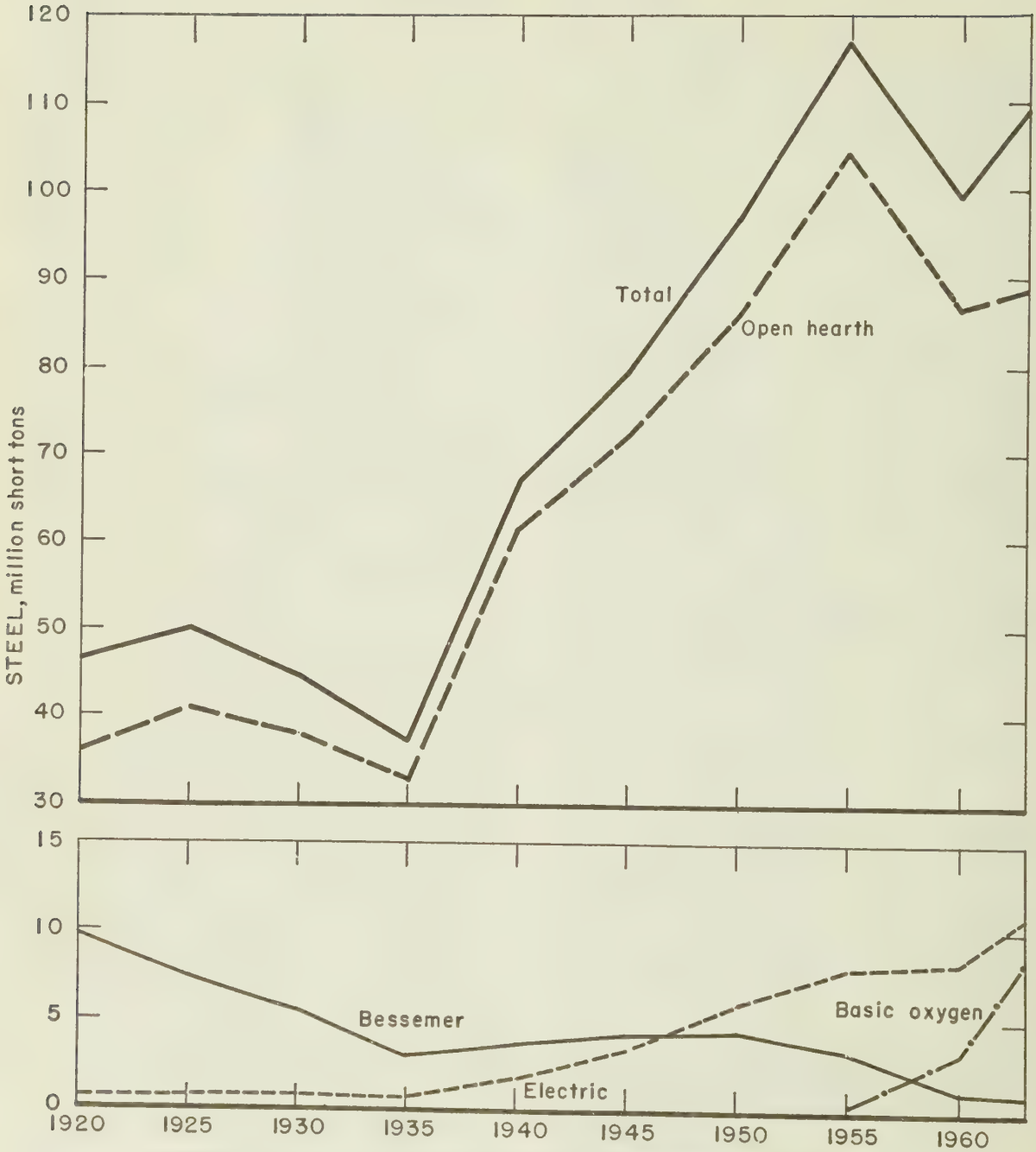

FIGURE 1.—Comparison of U.S. Steel Output by Various Steelmaking Processes.

Plants that do not operate blast furnaces utilize cold pig iron and some carbonaceous material or both. During subsequent refining of the heat nearly all the manganese, phosphorus, and silicon are oxidized and retained in the slag. Plans utilizing high-phosphorus pig iron (over 0.2 percent) use additional limestone in controlling phosphorus. Sulfur removal to the requirement of less than 0.05 percent is difficult with sulfur-containing raw materials, including fuels. Large slag volumes, high slag basicity, and fluid slags with good bath action tend to aid desulfurization. High temperatures also aid in sulfur removal.

TABLE 4.—*Fast heat times for basic oxygen process converters at Jones & Laughlin Steel Corp.*

	Aliquippa works	Cleveland works
Scrap charging time, minutes	2.0	1.0
Hot-metal charging time, do	1.0	1.0
Oxygen flow rate, cubic feet per minute	6,500	22,000
Oxygen blowing time, minutes	20.3	19.0
Charge-to-tap time, do	24.5	26.0
Tap-to-tap time, do	28.0	30.0
Heat size, tons	82.8	245.8
Rate, tons per hour	177.2	491.6
Charge ratio:		
Hot metal, percent	70.6	70.7
Scrap, do	28.8	29.3
Oxides, do	0.6	
Spar, pounds per ton	7.2	
Lance size, inches	2.05	3.50

Source: Journal of Metals, June 1964.

Oxygen steelmaking, which accounted for 12 percent of the steel produced in 1964, was introduced into the United States in 1954. There are two oxygen-converter steel processes used in the United States, the Linz-Donawitz (LD) process and the Stora-Kaldo process (see fig. 2). With one exception, all oxygen steelmaking in the United States is in LD furnaces. The LD process is the fastest known process for making high-quality, low-nitrogen steel. Heats of from 80 to 300 tons can be finished in 30 to 60 minutes from tap to tap. Tables 4 and 5 give data on various heats. This process is particularly adaptable to the usual run of basic pig iron produced in the United States. Its success depends upon the tonnage quantities of oxygen delivered to the furnace at low cost. The basic oxygen converter is a pear-shaped, tiltable vessel having a charging hole on top and a tapping hole near the top on one side. These converters range in size from outputs of 50 to 300 tons per heat. A typical 140-ton furnace shell is 22 feet 11 inches inside diameter, and 28 feet 1 inch high inside the shell. The diameter of the mouth opening is approximately 10 feet 2 inches inside the lining (*22*, *23*, *25*).

The first step in the production of the heat is the calculation of the amounts of hot metal, scrap, and fluxes to be charged to produce steel of the desired analysis, and the temperature at the conclusion of a predetermined oxygen flow.

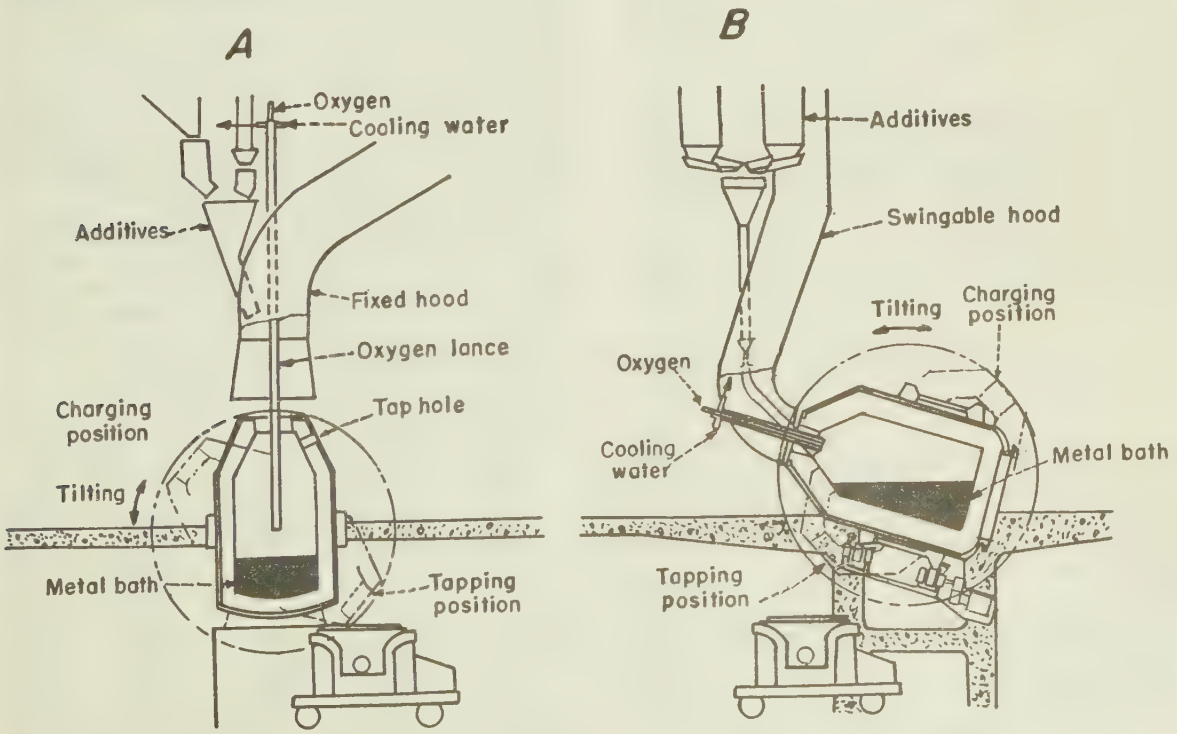

FIGURE 2.—Basic Oxygen Furnaces (A) Linz-Donawitz (B) Stora-Kaldo.

These calculations are based on the chemical analysis and temperature of the hot metal and include in the calculation the weight of the scrap, burnt lime, fluorspar, and the amount of oxygen to be used. Most steel mills using oxygen converters have them controlled with computers. After the calculations for the charge are made, scrap is dumped into the furnace first, immediately after this hot metal is added, the furnace is rotated upright, the oxygen lance is lowered, and the oxygen blow begins. Oxygen is blown into the furnace at supersonic speeds. Under normal operating conditions, the time elapse from the start of the charge of scrap to the start of the oxygen blow is from 3 to 5 minutes. Fluxes are added after the introduction of oxygen. At the conclusion of the blow steel samples are taken, the temperature noted, and adjustments can be made. If the melt is too hot, additional scrap can be put in for cooling; if the melt is too cool the oxygen lance is relowered and oxygen blown in for a short period. The furnace then is rotated to the tap hole side and molten steel poured into the teeming ladle. After the conclusion of the tap, the furnace is rotated in the opposite direction to dump slag in the cinder box. The furnace is then returned to the charging position ready to receive burden for the next heat. Total elapsed time from tap to tap is from 30 to 60 minutes, depending on size.

Refractory life has been improved. One source reports an average of 223 heats per lining for heats averaging 140 tons of steel. This is an average consumption of 15 pounds of brick per ton.

At first it was thought that the basic oxygen process was suitable only for regular low-carbon steel, but as operating efficiency increased the product includes practically the full spectrum of grades of steel.

The Stora-Kaldo process, the other oxygen steelmaking process used in this country, uses a tiltable converter similar in shape to the LD unit. However, during the steelmaking process the converter is inclined to about 17° from the horizontal and rotates on its longitudinal axis at speeds up to 30 rpm. One of the disadvantages of this process has been the extremely high consumption of refractories. Another small experimental converter, which may show promise in the future, is the Fuji circular converter. Pilot runs have used both a doughnut shape with a refractory island in the center, and a teacup shape with the island removed. In both installations a circular motion is imparted to the molten steel by the oxygen lances. The hot metal circulates at about two rotations per minute, and the slag blanket at a slower speed, thus there is a constant interaction between the hot metal surface and the slag as the metal flows in its circular path. This method effectively removes phosphorus and sulfur and leaves less oxygen and nitrogen than in open-hearth steel. In this method also there is a high rate of consumption of refractories (*25*).

Electric-furnace processes are used to make virtually all types of steel. The products include the entire range of stainless steels, high-alloy steels, high-speed and other alloy tool steels, low-alloy constructional steels, and plain carbon steels. Two types of electric furnaces are used in steelmaking, the arc type and the induction type (*13*, *17*).

Electric-arc furnaces are of the stationary or tilting design and vary in size of melts from a few hundred pounds to 200 tons. Although there are several types of arc furnaces, the most common is the direct arc in which the charge is melted by heat generated by the current arcing from the electrode to the bath. Table 6 shows the growth of electric arc furnaces with respect to size, power input, charging methods, and production rates in the United States.

Carbon is usually removed by oxidation to approximately the quantity desired in the finished steel. Sources of oxygen include iron oxide as ore, mill cinder, roll scale, and oxygen

TABLE 5.—*1964 operating data for Armco's Ashland basic oxygen shop*

	January	February	March	April	May
Number of heats	377	387	404	421	467
Average heat size, tons	149.7	150.3	149.9	150.6	154.17
Tap-to-tap, average hours per heat	1.53	1.24	1.11	1.09	1.01
Tap-to-tap, average tons per hour	98.01	121.14	135.30	137.86	154.17
Total operating hours	576.00	480.00	448.10	459.87	470.60
Hot metal charged, percent	73.19	78.20	76.08	75.00	74.61
Scrap charged, do	21.46	21.36	23.59	24.90	25.29
Other oxides charged, do				0.12	0.18
Burnt lime, pounds per ton	144.9	127.8	123.8	126.7	149.9
Spar, do	7.14	5.98	4.45	5.91	7.25
Other fluxes, do		12.4	20.4	14.3	5.2
Oxygen consumption, average cubic feet per ton	2,157	2,195	2,197	1,907	1,903
Oxygen blowing, cubic feet per minute	9,731	8,836	9,483	8,978	9,682
Yield, percent ingots	82.81	82.69	81.99	82.08	83.30
Heats under 0.10 carbon, percent	78.1	85.5	84.2	78.9	79.9
Heats 0.10–0.30 carbon, do	21.9	14.5	15.8	21.1	20.1

Source: Journal of Metals, August 1964.

TABLE 6.—*Developments in electric arc furnaces since 1918* [1] [2]

	1918	1925	1940	1950	1955
Diameter of shell	11 ft	16 ft–6 in	20 ft	20 ft	24 ft–6 in.
Size of heat—short tons	7	40	90	90	200
Length of heat, tap-to-tap	8 h	10 h	9 h.30 m	5 h.36 m	8 h.42 m.
Rate of production per hour—short tons	0. 875	4. 0	9. 5	16. 0	23. 0
Rating of transformer, kv.-a	2, 500	10, 000	12, 000	20, 000	25, 000 [3]
Diameter of electrode	17 in. carbon	18 in. graphite	20 in. graphite	20 in. graphite	24 in. graphite
Energy consumption—kw.-hr./ton	675	570	570	520	475
Type of charging	Door	Door	Door	Top	Top
Slag practice	Double	Double	Single	Single	Single

[1] All data pertain to 100-percent cold charges.
[2] King, C. D. (U.S. Steel Corp.). Steelmaking Processes—Some Future Prospects: J. Metals, April 1954, v. 6, No. 4, p. 465.
[3] Can be increased to 33,000 kv.-a. with heat exchangers.

injected through lances. When refining is completed, the heat is tapped into a ladle. To obtain the desired analysis, ferroalloys are added to the furnace before tapping, or in the ladle as the heat is being tapped. Aluminum or ferrosilicon is added if a deoxidized steel (semikilled or fully killed) is desired. If rimmed or mechanically capped steel is being made, small quantities of deoxidizers are used to control rimming action or ingot structure. As phosphorus and sulfur cannot be removed by the acid process, production of high-quality steel by this method requires raw materials with low impurities.

Selection of scrap charge (98 percent scrap, 2 percent pig iron U.S. average) of the electric furnace is made according to the grade of steel being produced. The furnace can be operated to permit highly efficient recovery of alloys by proper slag manipulation. Oxidizing and reducing slags may both be used in the same heat, depending on the composition of the charge and the analysis of the product. Limestone, lime, silica sand, crushed coke, aluminum, and fluorspar are materials used for slag constituents. The elimination of elements is the same as in the open hearth under basic oxidizing conditions. Sulfur may be removed from the metal with a reducing slag containing over 2 percent calcium carbide. In the presence of chromium, the removal of carbon is difficult because of the chemical affinity chromium has for carbon. Carbon may be absorbed by the metal while part of the chromium is being oxidized and going into the slag.

To oxidize carbon in a charge containing a high percentage of stainless-steel scrap requires an excess of oxygen and extremely high temperatures (over 3,200° F). Oxygen supplied through a lance into the molten bath is now used to a large extent instead of iron ore as the oxygen source. Oxidation of the metalloids is an exothermic reaction which reduces the energy requirements. With either source of oxygen considerable chromium is oxidized along with the carbon, and the resultant slag will contain a high percentage of chromium oxide. Chromium oxide may be reduced and returned to the metal by adding lime and crushed ferrosilicon.

The control of hydrogen in stainless steel is a frequent problem of many producers. Hydrogen may result from reducing moisture in the charge materials, water leaks in the furnace-cooled system, inadequately dried ladles, or high humidity in the atmosphere. When an appreciable quantity of hydrogen is absorbed in a stainless steel melt, it results in bleeding and porous ingots. Argon and helium gas and dry air are effective for purging hydrogen from the bath.

In an induction furnace, an electric current is induced in the metallic charge, causing it to become hot. Because of the action of the induced current, the metal bath is in constant circulation, and the swirling motion tends to homogenize the bath. The charge is carefully selected to produce the composition desired in the finished steel. Additions are mainly limited to small quantities of ferroalloys as final deoxidizers. Induction furnaces range in capacity from a few pounds up to 3 tons or more. Special steels and alloys, superior in quality to those produced by other methods of manufacture, may be produced in induction furnaces by melting in a vacuum or under pressure in an inert gas atmosphere. In such operations, the furnace and mold are enclosed in airtight containers, which can be evacuated or put under pressure with an inert gas. When the melting is complete, the crucible is tilted to pour molten metal into the ingot mold, and the metal solidifies under vacuum.

The Bessemer process was the first of the three processes used commercially in large-scale production of steel. A Bessemer converter is a pear-shaped vessel 10 feet or more high, open at the top, lined with acid refractory material,

and mounted on trunnions, so that it can be tilted to receive the hot metal and to pour the steel when a "blow" is finished.

Molten pig iron, 15 to 40 tons at a time, is poured into a Bessemer converter, and a blast of air is introduced from the bottom through a number of small openings in a specially designed base of refractory material. As the air is forced through the liquid metal, carbon and some of the undesirable elements, except phosphorus and sulfur, contained in the pig iron are oxidized and form slag constituents or escape as gases. The nitrogen content of Bessemer steel averages between 0.012 and 0.016 percent compared with 0.004 to 0.006 percent in the open-hearth process (*13*, *19*). The metalloids, particularly carbon, react with the ferrous oxide in the blown metal at high temperatures, and the gaseous product of reaction contributes to a lower inclusion content. Completely deoxidized steel, made by this method, is useful in such applications as pipe for structural purposes or where pipe is subjected to high pressures, because of its high yield-point and elastic-ratio characteristics (*21*). In addition to the steel tapped and teemed into ingot molds from the Bessemer converter, a considerable quantity is transferred while molten to tilting open-hearth furnaces for further refining. This is known as the duplex process.

Vacuum melting reduces gases and metals, decreases inclusions, and results in improved composition control. A comparison of the gas content of heat-resistant alloys by air melting and vacuum melting is given in table 7. Refractories are one of the problems in vacuum melting. For example, the oxygen level may increase after it has been reduced to low levels because of the oxygen contained in the refractories. Oxygen increases the loss of alloying elements to the slag; these elements also may remain in the steel as an oxide inclusion. Table 8 illustrates how vacuum melting removes metals, which may or may not be desirable,

TABLE 7.—*Decrease in gas content on consumable-electrode, vacuum remelting* [1]

Gas	Alloy	Air-melted electrode, ppm	Consumable electrode vacuum remelting, ppm	Decrease, percent
Hydrogen	Waspaloy	17.7	2.2	88
Do	M-252	16.0	1.7	89
Do	A-286	13.1	2.8	79
Oxygen	Waspaloy	31.0	2.0	94
Do	M-252	15.0	6.0	60
Do	A-286	13.0	5.0	62
Nitrogen	Waspaloy	420.0	120.0	71
Do	M-252	160.0	40.0	75
Do	A-286	300.0	20.0	93

[1] W. W. Dyrkacz. Vacuum Melting in the Steel Industry Today. J. Metals, v. 9, No. 12, December 1957, p. 1,515.

TABLE 8.—*Effect of vacuum melting on high-purity binary alloys* [1]

[One micron pressure and 1,600° C]

Elapsed time—minutes	Content, percent						
	0	5	10	20	40	60	90
Mn	0.6	>0.01	>0.01	>0.01	>0.01	>0.01	>0.01
Cr	0.63	0.58	0.54	0.51	0.51	0.51	0.51
Pb	0.94	0.021	0.011	0.005	0.003	0.002	0.002
Cu	0.92	0.27	0.08	0.014	0.005	0.004	0.002
P	1.13						1.10
Si	0.75	0.70	0.68	0.60	0.58	0.57	0.58
Ni	1.05						1.10
Sn	0.81	>0.01	>0.01	>0.01	>0.01	>0.01	>0.01
Zn	0.62	>0.01	>0.01	>0.01	>0.01	>0.01	>0.01

[1] Journal of The Iron and Steel Institute. The Behaviour of Various Elements in Vacuum Steelmaking. February 1959, pp. 172–175.

from steel. These data were determined from a series of binary alloys (iron plus up to 1 percent residual or alloying elements). One manufacturer claims that the life of a ball-bearing steel, AISI 52100, was increased by 400 percent when vacuum melted, as compared with conventional arc-melting methods.

Casting

Another innovation which is being adopted more slowly in the United States than oxygen steelmaking is continuous casting. In continuous casting the hot metal is teemed into a tundish of suitable design and the metal runs from this through nozzles into a water-cooled copper mold. This mold often has a vertical oscillation which prevents the freezing metal from solidifying to the mold. The casting has time to form only a thin skin while in contact with the mold, which is usually from 20 to 36 inches long, before it enters into the secondary cooling stage. This consists of jets of water played directly on the casting and may be from 10 to 30 feet long depending on the casting size, cross section, specific heat, and other factors.

Originally continuous casting machines were extremely high as it was a completely vertical process, but later, as shown in figure 4, machines have incorporated the use of bending rolls so that the casting, before it becomes cold, is rolled out horizontally. Some of the advantages claimed for continuous casting machines, besides lower capital investment and operating costs, are a greater yield of semifinished products from hot metal, elimination of ingot molds, hot tops, stripping cranes, soaking pits, and primary mills, and improvement on the internal quality of steel because of faster solidification, greatly improved surface quality through elimination of ingot casting and the primary mills (*21*). Table 9 gives a list of continuous casting plants in the United States.

TABLE 9.—*Continuous-casting plants, June 1, 1964*

Company	Location	Strands	Production	Steel grade
Armco Steel Corp	Butler, Pa			
Armco Steel Corp	Sand Springs, Okla	4	15,000 tons per month	Carbon.
Bethlehem Steel Co	Bethlehem, Pa	1		Do.
Copperweld Steel Co	Warren, Pa			
H. K. Porter Co., Inc. Connors Steel Div	Birmingham, Ala	4	650 tons per day	Carbon, low alloy.
Florida Steel Corp	Tampa, Fla			Carbon.
McLouth Steel Corp	Detroit, Mich	1		Do.
National Steel Corp	Weirton, W. Va	6	1,000,000 tons per year	Carbon, killed and rim.
Phoenix Steel Corp	Claymont, Del	2	300,000 tons per year	Alloy.
Roanoke Electric Steel Corp	Roanoke, Va	2	72,000 tons per year	Carbon.
Roblin Steel Corp	Dunkirk, N.Y	2	400 tons per day	Carbon, low alloy.
Soule Steel Co	Long Beach, Calif	2	36,000 tons per year	Carbon.
United States Steel Corp	Gary, Ind	1	1,500,000 tons per year	Do.
Wickwire Bros. Inc	Cortland, N.Y	3 ply		Do.

Source: Chemical Engineering, v. 71, No. 19, Sept. 14, 1964.

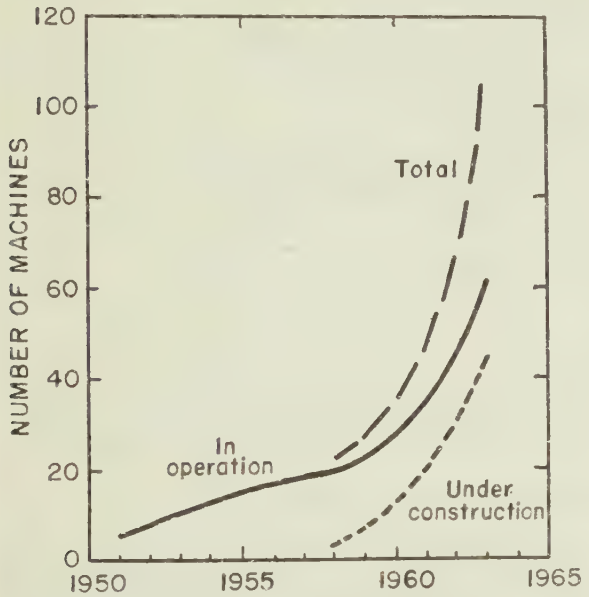

FIGURE 3.—Growth of Continuous Casting.

Pressure casting, which has been used for several years for railroad wheels, is also being more widely adopted by the industry. The principal advantage also of pressure casting is greater recovery of hot metal in final casting, and better surface control. A process being advocated to utilize the advantages of vacuum melting or casting, and the savings in continuous and pressure casting, is vacuum degassing. One type of operation consists of inserting a refractory nozzle extending from a vacuum vessel through the slag layer of a heat of steel in a conventional ladle. When vacuum is applied the amount of steel exposed is cycled by lowering and raising the vessel. This method was developed by Dortmund-Horder-Hutten Union (D–H). The other unit more recently introduced into this country is called Ruhrstahl-Heraeus (R–H). This unit has two refractory tubes extending from the vacuum chamber which dip below the surface of the molten metal. After vacuum jets have raised the liquid steel to a certain level in the tubes, argon, or other gasses, can be introduced through one tube. Advantages claimed for this method are—faster degassing time, minimum heat loss, and possibility of using reactive gasses in the vessel. Thus, hydrogen could be used instead of argon to further reduce oxygen levels (*25*).

USES

From 1959 through 1963 over 20 percent of the direct shipments of steel products went to the automotive industry. During this period direct shipments to the construction industry have averaged 16 percent and those to warehouse distribution centers have averaged 16 percent. Since the construction industry buys much of its steel from the warehouse distributors, it is probable that for the last few years the construction industry has been consuming about as much steel as the automotive industry. Steel for containers, packaging, and shipping materials has averaged over 9 percent of total shipments for the last 5 years. Steel for all kinds of industrial machinery, electrical machinery, appliances, and other domestic and commercial equipment accounted for about 14 percent of the shipments, leaving about 24 percent for shipbuilding, aircraft, oil and gas, mining, agriculture, ordnance, and export. Table 10 gives distributions of steel for consumption by market classifications (*5*).

Steel service centers, warehouses, and distributors get about 13 million tons of steel shipped directly to them. This is distributed to almost all of the other consumer markets, therefore, it is difficult to assign certain amounts to various market classifications. For the last decade the percentages of steel used have remained about the same for the various market classifications.

The improvements that have been made in steel make it difficult to make good comparisons by weight since, with new alloys, lighter weight

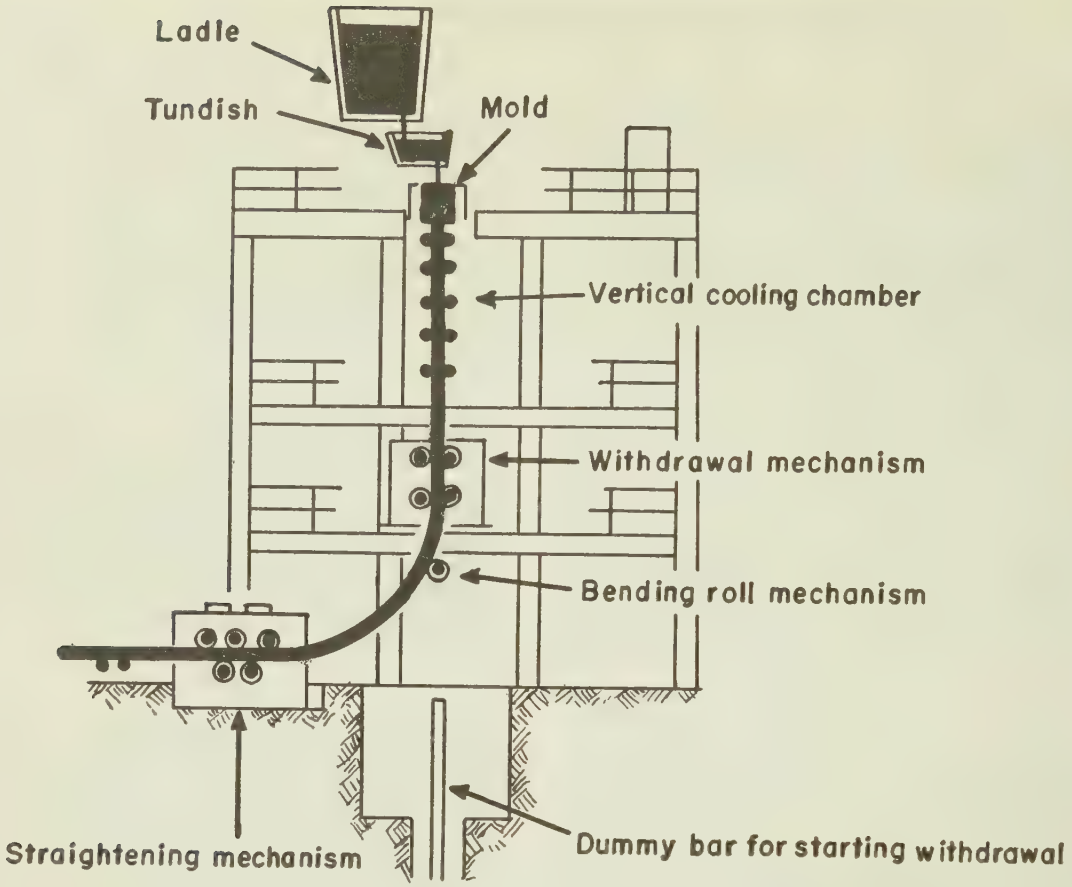

FIGURE 4.—A Vertical Continuous Casting Machine With Bending Rolls.

TABLE 10.—*Domestic shipments of steel products by market classifications, 1963*

	Thousand short tons	Percent
For converting and processing	2,612	3.5
Forgings (other than automotive)	899	1.2
Bolts, nuts, rivets and screws	1,160	1.6
Warehouses and distributors [1]	13,149	17.8
Construction, including maintenance	10,051	13.6
Contractors products	4,339	5.9
Automotive	16,889	22.9
Rail transportation	2,563	3.5
Shipbuilding and marine equipment	712	1.0
Aircraft	77	.1
Oil and gas drilling	295	.4
Mining, quarrying, and lumbering	284	.4
Agricultural	1,225	1.7
Machinery, industrial equipment and tools	4,498	6.1
Electrical machinery and equipment	2,284	3.1
Appliances, utensils, and cutlery	2,010	2.7
Other domestic and commercial equipment	1,892	2.6
Containers	6,464	8.7
Ordnance and other military	289	.4
Nonclassified shipments	2,032	2.8
Total	73,724	100.0

[1] Products are distributed to the various other industries shown in this table as well as hardware stores and other users. Data on the quantity shipped to each of these industries are not available.

Source: American Iron and Steel Institute.

steels now do the same job as heavier steels did formerly. Thus steel company research led to the development of a new high-strength linepipe of larger diameter, that has greater resistance to corrosion. This allows for the transportation of more gas and oil for longer distances under greater pressure with less steel. Similarly for containers the steel industry is now making tin plate much thinner. This increases the total overall advantage as the lighter-weight stronger steel products have greater corrosion resistance and therefore longer life. As these advantages combined with lower transportation costs become more evident, the per capita consumption of steel will start to rise gradually.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Coke byproducts and their derivatives number in the hundreds but principally comprise coke breeze, coke-oven gas, tar, ammonium sul-

fate, ammonium liquor, and light oils. Coke breeze is used for agglomerating iron ore, and coke-oven gas is used as a fuel for heating coke ovens in steelmaking and reheating furnaces. Useful products from light oils vary from benzene to xylene. A recent development in coke-plant technology is the removal of hydrogen from coke-oven gas. The recovered hydrogen is used in manufacturing ammonia.

Blast-furnace gas and slag are byproducts of blast furnaces. Blast-furnace gas is used for heating coke ovens, blast-furnace stoves, steel furnaces, and power generation. Blast-furnace slag is used as aggregate ballast for railroads, in manufacture of cement, mineral wool, sewerage filtration, agriculture, and for many other purposes. The annual value of blast-furnace slag produced in the United States is $40 to $50 million. In addition, approximately 8 million tons of flue dust is recovered annually, which is used in making sinter or is charged directly into the blast furnace.

The main byproduct of steelmaking furnaces that is reused is open-hearth slag which is utilized as a source of manganese and flux (calcium and magnesium) in blast furnaces. Some 5 million tons goes annually for this purpose. In addition, several million tons of iron is recovered from slag dumps annually and is used in blast and steelmaking furnaces. In the Birmingham, Ala., area, open-hearth slag from the duplex process of the Ensley plant is employed as a soil conditioner because of its available phosphorus. Iron recovered from electrostatic precipitators installed at open-hearth and oxygen furnaces is agglomerated and charged back into blast and steel furnaces. In addition, the majority of open-hearth plants generate a considerable part of their electrical energy requirements from waste-heat boilers.

Steel scrap (20 to 30 percent of ingot output) is generated in rolling mills through the cropping of blooms and slabs and other shearing necessary to remove defects and meet size specifications. This material constitutes home scrap. There is a 2- to 3-percent scale (iron oxide) loss everytime that steel is heated for rolling. This scale may be charged directly into blast furnaces or be used in steelmaking furnaces. When used in steelmaking furnaces, it is a source of metallics and oxygen for refining the melt.

ALTERNATE MATERIALS

Metals and nonmetals competing with steel have captured some of the market when steel was in short supply; but its versatile properties and relatively low cost makes steel still the most prominent material for structural applications and other purposes in use today. The principal competing materials are aluminum, plastics, glass, and concrete.

Research to improve steel, to modify or combine it with other materials, and to adapt it to the end product has resulted in its resurgence. Steel products have become lighter, stronger, and more corrosion resistant, thus displacing substitutes such as aluminum in the automotive market, which is steel's biggest market. Steel panels coated with colored plastics are being used in construction. New rolling techniques make steel much thinner and more practical for foil and containers. Better alloy steels of higher strength are recapturing some of the structural market leading to revision of building codes to accept these lighter, stronger steels. Steel pipe is coated with plastic to resist corrosion or lined with glass to carry corrosive materials.

The steel industry is putting greater emphasis on market research and product development for the consumer. Many of the materials formerly regarded as substitutes have been incorporated into the design of new steel products to modify or improve the characteristics of the steel.

SECONDARY SOURCES AND RECOVERY (11)

Ferrous scrap comprises over half of all the metallics charged into iron and steelmaking furnaces in the United States. In recent years the proportion of scrap used has decreased, partly because of the use of oxygen in steelmaking furnaces, but the importance of recycling 65 to 75 million tons of metal a year as a secondary raw material cannot be overlooked. The presence of contaminant metals as alloying elements in scrap has been a positive deterrent to its use, but it is felt that the development of metallurgical separation methods will supplement the huge scrap metal disintegrators recently introduced to remove contaminating materials. Table 11 gives the proportion of iron and steel scrap and pig iron used in furnaces in the United States at 5 year intervals since 1953, while table 12 shows the consumption in short tons of iron and steel scrap by the type of manufacture and by the grade of scrap in 1963.

CONSERVATION

Conservation of the metal represented by creation of 75 million tons of steel products annually is extremely important from a raw material and waste disposal standpoint. Hot metal, molten iron of known composition, is the most satisfactory raw material for steelmaking, but

TABLE 11.—*Proportion of iron and steel scrap and pig iron used in furnaces in the United States*

[Percent]

Type of furnace	1953		1958		1963	
	Scrap	Pig iron	Scrap	Pig iron	Scrap	Pig iron
Open-hearth	44.8	55.2	41.5	58.5	41.5	58.5
Basic oxygen converter					28.2	71.8
Bessemer	6.0	94.0	[1] 19.3	[1] 80.7	8.9	91.1
Electric	98.1	1.9	[2] 96.9	[2] 3.1	98.4	1.6
Cupola	65.7	34.3	70.0	30.0	76.8	23.2
Air	79.3	20.7	82.9	17.1	88.1	11.9
Crucible	33.3	66.7				

[1] Includes oxygen-steel process.

[2] Includes crucible furnaces.

TABLE 12.—*Consumption of iron and steel scrap by type of manufacturer, by grades, in 1963*

[Thousand short tons]

Grades of scrap	Steel ingots and castings	Steel castings	Iron foundries and miscellaneous users
Steel scrap, excludes rerolling rails:			
Carbon	51,206	2,560	3,826
Alloy, excludes stainless	2,399	127	129
Stainless	666	29	22
Cast iron, includes borings	5,020	338	8,299
Total	59,291	3,054	12,276

the steel in scrap is an alloy of iron with other elements. This represents a serious drawback in the conservation of steel products. As these alloys become more complex the elimination of the alloying or contaminating element becomes more difficult. The necessity for work on the conservation of steel has been highlighted in recent years by the increasing numbers of scrap automobile bodies that have been stripped of useful components and remain as small steel jungles, lowering the use value of the property that they are on and destroying the aesthetic values of the surrounding property.

SOURCES OF STATISTICAL INFORMATION

Steel-ingot-production data are published by the American Iron and Steel Institute, and pig iron production and consumption of pig iron and ferrous scrap are published by the Bureau of Mines. Statistics on the production of steel ingots and steel castings by ingot producers and independent foundries are provided by the Bureau of the Census. Data on the production of iron castings are not published by any association or Government agency. The Bureau of the Census publishes monthly statistics on shipments of iron castings.

Statistics on the supply and consumption of iron and steel scrap are collected and published monthly by the Bureau of Mines. These data are also collected by the American Iron and Steel Institute for the steel industry, which excludes the noncaptive foundries and other miscellaneous users.

PRODUCTION, CONSUMPTION, AND TRADE

Domestic production of iron and steel in 1963 accounted for about 26 percent of the world estimated production of steel ingots and castings. Tables 13 to 16 show salient iron and steel statistics and domestic and world production of pig iron and steel. U.S. imports and exports of iron and steel products are given in tables 17 and 18.

Production of steel by the new basic oxygen process has grown fourfold since 1958 at the expense of other methods of manufacture, and in 1963 accounted for about 8 percent of the domestic output.

Imports and exports constitute only a small part of the total domestic supply and demand for pig iron, scrap and steel. However, large quantities of certain products such as sheets and plate, structural iron and steel, rods (wire, nail, and flat) and steel pipe and tubing are imported for consumption. Data on the quantity of steel used by the various consuming industries are given in the section on Uses.

Tariff rates on iron and steel products vary with the type of product and composition (particularly alloy content); how manufactured, hot or cold rolled, cast or forged, coated or clad. Typical duty rates on some iron and steel products are shown in table 19. On some iron products containing *chromium*, *molybdenum*, *tungsten*, or *vanadium* over a specified quantity, additional duties are applicable. These rates are shown in table 20 (*26*, *27*).

TABLE 13.—*Salient iron and steel statistics*

[Thousand short tons]

	1954–58 (average)	1959	1960	1961	1962	1963
United States:						
Pig iron:						
Production	69,077	60,210	66,501	64,853	65,638	71,840
Shipments	68,800	61,245	65,612	65,307	65,727	72,211
Imports for consumption	267	700	331	377	500	645
Exports	260	10	112	416	154	70
Steel:						
Production of ingots and castings (all grades):						
Carbon	94,955	84,539	90,862	89,338	89,160	98,714
Stainless	1,055	1,131	1,004	1,137	1,085	1,204
All other alloy	7,697	7,776	7,416	7,539	8,083	9,343
Total	103,707	93,446	99,282	98,014	98,328	109,261
Total shipments of steel mill products	74,186	69,377	71,149	66,126	70,552	75,555
Imports for consumption of major iron and steel products	1,308	4,615	3,570	3,308	4,297	5,582
Exports of major iron and steel products	4,281	1,973	3,247	2,221	2,266	2,664
World production:						
Pig iron (includes ferroalloys)	209,970	247,230	285,270	282,370	291,820	308,970
Steel ingots and castings	293,580	336,510	381,560	386,780	396,260	425,310

Source: American Iron and Steel Institute.

TABLE 14.—*Steel production in the United States, by type of furnace* [1]

[Thousand short tons]

Year	Open hearth		Bessemer	Basic oxygen process	Electric [2]	Total
	Basic	Acid				
1954–58 (average)	92,685	528	2,594	[3] 488	7,412	103,707
1959	81,225	444	1,380	1,864	8,533	93,446
1960	85,964	404	1,189	3,346	8,379	99,282
1961	84,108	394	881	3,967	8,664	98,014
1962	82,578	379	805	5,553	9,013	98,328
1963	88,437	397	963	8,544	10,920	109,261

[1] Includes only that steel for castings produced in foundries operated by companies manufacturing steel ingots. Omits about 2 percent of total steel production.
[2] Includes crucible, oxygen converter steel, 1954–55.
[3] Data for 3-year period only.

Source: American Iron and Steel Institute.

STRATEGIC CONSIDERATIONS

Steel is essential to civilian uses and defense purposes. Plants are relatively widely dispersed even though most of them are concentrated in the northeastern part of the United States. Nevertheless, several plants must receive strategic considerations because of their size.

In 1963, the five largest steel companies in the United States had 59 percent of the total industry sales. They are as widely dispersed as is economically feasible and their general concentration in the States bordering the Great Lakes gives them the advantage of a broad waterway for the transportation of raw materials. The United States is self-sufficient in iron for steel but not in all of the alloying elements used. See production of steel, by States, in table 1.

GOVERNMENT PROGRAMS

The steel industry is not subject to any defense programs and is only concerned with the effect of the stockpiling program on metals used in alloys. The Bureau of Mines has an experimental blast furnace which it is operating in cooperation with the steel industry. The Bureau, through its Mineral Resource Offices, has been studying the generation and movement of ferrous scrap throughout the United States, and has been given a large role in the waste utilization study which is a part of the large beautification program for the United States.

PRICES AND COSTS

The domestic steel industry uses f.o.b. mill prices for all its steel products. The following tabulation gives 1964 prices of steel, pig iron, and scrap: [3]

Composite finished steel	$0.06368 per pound
Pig iron composite	63.11 per long ton
Steel scrap, heavy-melting composite	33.67 per long ton

[3] Iron Age.

TABLE 15.—*World production of pig iron (including ferroalloys) by countries* [1] [2]

[Thousand short tons]

Country [1]	1954–58 (average)	1959	1960	1961	1962	1963
North America:						
Canada	3, 327	4, 318	4, 436	5, 064	5, 427	6, 059
Mexico	425	635	756	864	912	947
United States	71, 294	62, 135	68, 620	66, 717	67, 636	73, 853
Total	75, 046	67, 088	73, 812	72, 645	73, 975	80, 859
South America:						
Argentina	36	39	198	437	438	[3] 49
Brazil	1, 333	1, 750	1, 965	2, 050	2, 064	[3] 2, 205
Chile	356	320	293	314	422	461
Colombia	131	160	204	208	164	223
Venezuela	----------	----------	----------	6	136	333
Total	1, 856	2, 269	2, 660	3, 015	3, 224	[3] 3, 717
Europe:						
Austria	1, 846	2, 028	2, 467	2, 500	2, 339	2, 326
Belgium	5, 925	6, 575	7, 223	7, 104	7, 439	7, 622
Bulgaria	37	195	212	227	246	222
Czechoslovakia	3, 613	4, 679	5, 176	5, 480	5, 732	5, 792
Denmark	56	64	76	73	76	[3] 75
Finland	115	119	151	168	377	413
France	12, 312	13, 951	15, 921	16, 372	15, 619	15, 985
Germany:						
East	1, 730	2, 092	2, 199	2, 239	2, 287	2, 370
West (including Saar)	19, 369	23, 814	28, 372	28, 033	26, 732	25, 253
Hungary	980	1, 217	1, 373	1, 440	1, 523	1, 530
Italy	2, 082	2, 416	3, 113	3, 528	4, 054	4, 264
Luxembourg	3, 494	3, 795	4, 173	4, 226	3, 965	3, 954
Netherlands	785	1, 259	1, 485	1, 606	1, 732	1, 884
Norway	472	686	794	834	797	821
Poland	3, 709	4, 822	5, 030	5, 258	5, 854	5, 947
Portugal	[3] [4] 20	40	45	134	248	276
Rumania	662	933	1, 118	1, 211	1, 666	1, 881
Spain	1, 144	1, 889	2, 124	2, 340	2, 374	2, 194
Sweden	1, 458	1, 657	1, 799	2, 094	2, 014	2, 075
Switzerland	47	[3] 50	[3] 60	[3] 60	[3] 60	49
U.S.S.R. [5]	38, 730	47, 368	51, 541	56, 100	60, 919	64, 706
United Kingdom	14, 511	14, 092	17, 655	16, 517	15, 335	16, 342
Yugoslavia	676	995	1, 123	1, 161	1, 216	1, 168
Total	113, 773	134, 736	153, 230	158, 705	162, 604	167, 149
Asia:						
China	[6] 5, 800	[6] 22, 600	30, 300	[3] 16, 500	[3] 16, 500	[3] 18, 700
India	2, 201	3, 519	4, 705	5, 621	6, 522	7, 431
Japan	6, 899	10, 908	13, 604	18, 059	20, 325	22, 525
Korea:						
North	247	765	940	1, 025	1, 337	[3] 1, 280
Republic of	----------	9	15	10	----------	[3] 6
Taiwan (Formosa)	17	36	26	58	69	60
Thailand	3	8	7	6	6	7
Turkey [7]	235	260	272	260	323	233
Total [5]	15, 402	38, 105	49, 869	41, 539	45, 082	50, 242
Africa:						
Southern Rhodesia	71	79	95	243	266	276
South Africa, Republic of	1, 513	1, 992	2, 204	2, 566	2, 680	2, 691
United Arab Republic (Egypt)	[8] 17	130	163	[3] 110	[3] 110	----------
Total	1, 601	2, 201	2, 462	2, 919	3, 056	2, 967

See footnotes at end of table.

TABLE 15.—*World production of pig iron (including ferroalloys) by countries* [1] [2]—Continued

[Thousand short tons]

Country [1]	1954–58 (average)	1959	1960	1961	1962	1963
Oceania: Australia [9]	2, 288	2, 829	3, 240	3, 549	3, 879	[10] 4, 032
World total (estimate)	209, 970	247, 230	285, 270	282, 370	291, 820	308, 970

[1] Pig iron is also produced in Republic of the Congo, but quantity produced is believed insufficient to affect estimate of world total.
[2] This table incorporates some revisions. Data do not add to totals shown due to rounding where estimated figures are included in the detail.
[3] Estimate.
[4] One year only as 1958 was the first year of commercial production.
[5] U.S.S.R. in Asia included with U.S.S.R. in Europe.
[6] Based on figures from Chinese sources. 1958 does not include approximately 4,000,000 tons produced of sub-standard grade iron produced at small plants. 1959 production probably includes pig iron obtained from reworking the low-grade product of 1958 and an unreported quantity (probably relatively small) of sub-standard iron from small plants most of which were shut down early in the year.
[7] Includes foundry iron through 1962.
[8] Average annual production 1955–58.
[9] Includes scrap.
[10] Excludes ferroalloys.

TABLE 16.—*World production of steel ingots and castings by countries* [1]

[Thousand short tons]

Country [1]	1954–58 (average)	1959	1960	1961	1962	1963
North America:						
Canada	4, 492	5, 901	5, 790	6, 466	7, 173	8, 190
Mexico	955	1, 473	1, 657	1, 882	1, 896	2, 235
United States [2]	103, 707	93, 446	99, 282	98, 014	98, 328	109, 261
Total	109, 154	100, 820	106, 729	106, 362	107, 397	119, 686
South America:						
Argentina	290	236	305	486	711	987
Brazil	[3] 1, 519	2, 072	2, 530	2, 756	[4] 2, 870	[4] 2, 980
Chile	381	457	465	400	546	539
Colombia	88	121	173	194	151	219
Peru	[5] 22	56	66	83	79	80
Venezuela	[4] 55	[4] 55	52	83	248	401
Total	2, 355	2, 997	3, 591	4, 002	4, 605	5, 206
Europe:						
Austria	2, 305	2, 769	3, 487	3, 418	3, 274	3, 249
Belgium	6, 509	7, 096	7, 923	7, 728	8, 115	8, 294
Bulgaria	140	254	279	375	466	508
Czechoslovakia	5, 357	6, 764	7, 460	7, 764	8, 421	8, 375
Denmark	269	322	349	356	405	396
Finland	207	262	285	305	335	346
France	14, 306	16, 617	18, 907	19, 211	19, 004	19, 353
Germany:						
East	2, 980	3, 535	3, 678	3, 796	3, 993	3, 997
West (including Saar)	25, 608	32, 446	37, 589	36, 881	35, 895	34, 830
Greece	85	99	[4] 140	[4] 150	[4] 170	[4] 180
Hungary	1, 661	1, 939	2, 080	2, 263	2, 572	2, 617
Ireland	32	44	44	31	21	22
Italy	6, 299	7, 454	9, 071	10, 283	10, 755	11, 195
Luxembourg	3, 611	4, 038	4, 502	4, 534	4, 420	4, 445
Netherlands	1, 231	1, 841	2, 141	2, 173	2, 301	2, 582
Norway	288	470	540	550	539	599
Poland	5, 369	6, 790	7, 585	7, 974	8, 470	8, 823
Rumania	875	1, 565	1, 991	2, 344	2, 702	2, 981
Spain	1, 469	1, 995	2, 157	2, 579	2, 547	2, 606
Sweden	2, 481	3, 155	3, 547	3, 922	3, 982	4, 297
Switzerland [6]	213	276	303	327	351	342
U.S.S.R. [7]	53, 242	66, 107	71, 973	77, 990	84, 106	88, 427
United Kingdom	22, 452	22, 609	27, 222	24, 737	22, 950	25, 222
Yugoslavia	987	1, 432	1, 590	1, 689	1, 758	1, 750
Total [7]	157, 976	189, 879	214, 843	221, 380	227, 552	235, 436

See footnotes at end of table.

TABLE 16.—*World production of steel ingots and castings by countries*[1]—Continued

[Thousand short tons]

Country[1]	1954–58 (average)	1959	1960	1961	1962	1963
Asia:						
China	5,050	[8] 14,720	[8] 20,340	10,500	11,000	13,000
India	1,939	2,726	3,623	4,488	5,635	6,576
Israel	[9] 14	26	44	68	88	74
Japan	11,673	18,330	24,403	31,160	30,364	34,724
Korea:						
North	226	497	707	855	1,157	1,127
Republic of	13	42	55	73	163	176
Taiwan (Formosa)	80	175	220	218	201	303
Thailand	4	7	8	9	8	[4] 8
Turkey	195	236	292	312	267	365
Total[7]	19,194	36,759	49,692	47,683	48,883	56,353
Africa:						
Southern Rhodesia	62	51	95	101	88	55
South Africa, Republic of	1,804	2,091	2,328	2,738	2,903	3,124
United Arab Republic (Egypt)[4]	103	110	150	165	165	410
Total	1,969	2,252	2,573	3,004	3,156	3,589
Oceania: Australia	2,934	3,803	4,137	4,351	4,667	5,040
World total (estimate)	293,580	336,510	381,560	386,780	296,260	425,310

[1] This table incorporates some revisions. Data do not add exactly to totals shown because of rounding where estimated figures are included in the detail.
[2] Data from American Iron and Steel Institute. Excludes production of castings by companies that do not produce steel ingots.
[3] Includes iron castings.
[4] Estimate.
[5] One year only as 1958 was the first year of commercial production.
[6] Including secondary.
[7] U.S.S.R. in Asia included with U.S.S.R. in Europe.
[8] Claimed figures. Data appear to be exaggerated by one-fifth or more.
[9] Average annual production 1957–58.

TABLE 17.—*U.S. imports for consumption of major iron and steel products*

Products	1962		1963	
	Short tons	Value	Short tons	Value
Iron products:				
Bar iron, iron slabs, blooms, or other forms	211	$64,710	265	$87,906
Pipes and fittings:				
Cast-iron pipe and fittings	35,540	4,043,946	37,949	4,117,651
Malleable cast-iron pipe fittings	3,325	1,304,389	3,936	1,534,890
Castings and forgings	15,056	5,220,909	22,258	7,606,168
Total	54,132	10,633,954	64,408	13,346,615
Steel products:				
Steel bars:				
Concrete reinforcement bars	607,024	44,284,929	545,203	39,254,792
Solid and hollow, n.e.s	126,356	17,012,239	206,839	19,504,819
Hollow and hollow drill steel	2,567	1,188,238	2,173	975,144
Wire rods, nail rods, and flat rods up to 6 inches in width	644,271	61,985,868	800,994	76,606,414
Boiler and other plate iron and steel, n.e.s	216,570	26,399,846	(1)	(1)
Steel ingots, blooms, and slabs; billets, solid and hollow	174,372	13,545,558	260,355	24,831,885
Die blocks or blanks, shafting, etc	2,100	828,928	1,757	664,005
Circular saw plates	54	67,991	[2] 146	[2] 70,639
Sheets of iron or steel, common, or black and boiler or other plate of iron or steel	215,179	26,261,302	(1)	(1)
Sheets and plates and steel n.s.p.f	10,976	4,669,932	1,018,299	121,688,057
Tinplate, terneplate, and taggers' tin	52,479	8,586,908	82,941	14,197,413
Structural iron and steel	708,795	74,872,972	933,075	89,203,358
Rails for railways	10,560	905,247	6,759	936,452
Rail braces, bars, fishplates, or splice bars and tie plates	268	29,123	638	67,260
Steel pipes and tubes	635,615	93,414,620	735,463	103,685,865

See footnotes at end of table.

TABLE 17.—*U.S. imports for consumption of major iron and steel products*—Continued

Products	1962		1963	
	Short tons	Value	Short tons	Value
Steel products—Continued				
Wire:				
Barbed	66,598	$8,762,116	90,029	$11,522,607
Round wire, n.e.s	242,250	44,608,626	277,874	49,707,055
Telegraph, telephone, etc. except copper, covered with cotton jute, etc	781	357,761	1,751	1,012,236
Flat wire and iron and steel strips	86,366	17,337,359	99,607	23,107,292
Rope and strand	39,323	11,958,768	47,561	13,610,182
Galvanized fencing wire and wire fencing	73,042	9,641,734	50,762	6,887,012
Iron and steel used in card clothing	(3)	241,391	(3)	349,694
Hoop and band iron and steel, for baling	24,694	3,174,978	27,707	3,701,291
Hoop, band and strips, or scroll iron or steel, n.s.p.f.	12,909	2,265,682	11,714	2,229,591
Nails	281,807	40,085,434	308,274	41,297,304
Steel castings and forgings	8,384	1,490,612	7,443	1,636,589
Total	4,243,340	513,978,162	5,517,364	646,746,956
Advanced manufactures:				
Bolts, nuts, and rivets	67,934	20,096,908	70,403	20,227,151
Chains and parts	9,506	6,102,429	9,243	6,200,689
Hardware, builders	----------	2,961,011	----------	2,748,845
Hinges and hinge blanks	----------	1,875,449	----------	2,014,423
Screws (wholly or chiefly of iron or steel)	----------	3,137,480	----------	3,629,403
Tools	----------	20,071,345	----------	18,672,207
Other	----------	1,550,041	----------	923,728
Total	----------	55,794,663	----------	54,416,446
Grand total	----------	580,406,779	----------	714,510,017

[1] Due to changes in classification of iron and steel plates by the Bureau of the Census, all classes of iron and steel plates and sheets for this table have been tabulated under "sheets and plates and steel n.s.p.f.," for 1963.

[2] Data are Jan.–Aug.; effective Sept. 1, 1963 saws were reported in number, Sept.–Dec., 127250 ($181,280).

[3] Weight not recorded.

Source: Bureau of the Census.

TABLE 18.—*U.S. exports of major iron and steel products*

Products	1962		1963	
	Short tons	Value	Short tons	Value
Semimanufactures:				
Steel ingots, blooms, billets, slabs, and sheet bars	252,998	$20,526,277	304,516	$24,665,086
Iron and steel bars, and rods:				
Carbon-steel bars, hot-rolled, and iron bars	52,491	9,682,725	47,269	9,105,344
Concrete reinforcement bars	22,398	2,950,860	46,009	6,016,137
Other steel bars	27,731	12,037,785	24,901	12,352,386
Wire rods	17,006	3,853,784	24,033	4,145,703
Iron and steel plates, sheets, skelp, and strips:				
Plates, including boilerplate, not fabricated	119,856	26,187,475	139,483	26,389,591
Skelp iron and steel	11,528	1,121,853	2,482	234,626
Iron and steel sheets, galvanized	124,692	25,046,171	108,282	21,601,977
Steel sheets, black, ungalvanized	458,073	102,825,501	457,610	114,057,783
Strip, hoop, band, and scroll iron and steel:				
Cold-rolled	33,196	15,784,152	37,732	17,625,323
Hot-rolled	31,617	6,779,069	51,297	11,260,004
Tinplate and terneplate	329,852	53,011,244	342,363	51,059,805
Tinplate circles, cobbles, strip, and scroll shearbutts	24,633	2,756,006	23,355	2,489,110
Total	1,506,071	282,562,902	1,609,332	301,002,875

TABLE 18.—*U.S. exports of major iron and steel products*—Continued

Products	1962		1963	
	Short tons	Value	Short tons	Value
Manufactures-steel mill products:				
Structural iron and steel:				
Water, gas, and other storage tanks (unlined), complete and knockdown material	20,468	$8,611,680	21,031	$9,759,863
Structural shapes:				
Not fabricated	145,702	20,841,902	154,229	22,975,571
Fabricated	58,817	29,474,702	169,750	37,052,602
Plates and sheets, fabricated, punched, or shaped	15,945	5,429,148	16,463	5,645,433
Metal lath	1,215	479,552	1,163	477,968
Frames, sashes, and sheet piling	13,881	2,940,590	8,235	1,953,252
Railway-track material:				
Rails for railways	102,191	12,922,089	44,045	5,970,153
Rail joints, splices bars, fishplates, and tieplates	19,921	4,645,589	45,323	9,183,035
Switches, frogs, and crossings	3,816	1,158,206	3,867	1,582,820
Railroad spikes	381	110,574	3,436	1,071,737
Railroad bolts, nuts, washers, and nut locks	881	445,877	6,023	1,429,887
Tubular products:				
Boiler tubes	10,470	7,573,794	11,840	8,066,150
Casing and line pipe	86,083	27,581,701	122,520	34,501,999
Seamless black and galvanized pipe and tubes, except casing, line and boiler, and other pipes and tubes	32,077	8,699,114	42,553	12,074,972
Welded black pipe	10,158	3,097,688	7,357	2,069,338
Welded galvanized pipe	5,609	1,305,537	12,017	2,610,468
Malleable-iron screwed pipe fittings	1,192	1,389,825	1,279	1,308,765
Cast-iron pressure pipe and fittings	22,630	4,209,718	119,397	15,450,543
Cast-iron soil pipe and fittings	6,373	1,651,629	7,246	1,803,201
Iron and steel pipe, fittings, and tubing, n.e.c.	50,205	41,929,545	58,743	46,352,732
Wire and manufactures:				
Barbed wire	12,896	2,685,658	23,178	4,294,517
Galvanized wire	10,108	3,116,705	22,492	6,025,095
Iron and steel wire, uncoated	16,206	5,504,412	21,477	6,956,824
Spring wire	1,469	986,920	1,418	915,333
Wire rope and strand	9,553	5,332,085	9,227	5,042,761
Woven-wire screen cloth	1,956	[1] 2,031,332	1,540	[1] 2,138,642
All other	15,591	9,680,812	17,160	10,798,742
Nails and bolts, iron and steel, n.e.c.:				
Wire nails, staples, and spikes	3,591	2,969,254	4,348	3,587,563
Bolts, screws, nuts, rivets, and washers, n.e.c.	15,025	19,210,961	19,580	22,465,248
Tacks	692	455,429	671	455,958
Castings and forgings: Iron and steel, including car wheels, tires, and axles	64,425	24,575,538	76,766	25,533,033
Total	759,527	261,047,566	1,054,374	309,554,205
Advanced manufactures:				
Building (prefabricated and knockdown)	----------	7,849,479	----------	6,458,148
Chains and parts	7,993	10,069,098	8,189	11,201,215
Construction material	9,264	6,598,605	8,099	5,888,865
Hardware and parts	----------	23,563,072	----------	24,422,387
House-heating boilers and radiators	----------	6,666,330	----------	6,197,711
Oil burners and parts	----------	8,856,731	----------	9,712,142
Plumbing fixtures and fittings	----------	2,701,981	----------	4,987,304
Tools	----------	59,146,072	----------	39,725,808
Utensils and parts (cooking, kitchen, and hospital)	----------	3,774,726	----------	3,298,068
Other	----------	45,447,634	----------	53,391,629
Total	----------	174,673,728	----------	165,283,277
Grand total	----------	718,284,196	----------	775,840,357

[1] Includes wire cloth as follows: 1962, $1,455,917 (7,463,741 square feet); 1963, $1,638,819 (3,404,155 square feet).

Source: Bureau of the Census.

The composite finished steel price as quoted from Iron Age is computed on the base of the following 10 carbon-steel products: Hot-rolled bars, structural shapes, plates, rails, pipe, wire, and hot- and cold-rolled sheets and strip. Although scrap prices formerly fluctuated widely the extensive development by integrated steel mills of their own iron ore facilities in the decade after World War II reduced the volume of scrap used by the steel industry and therefore reduced the extent of price fluctuations. Greater use of hot metal and the advent of the basic-oxygen converters further depressed the use of scrap, especially the lower grades. The composite price of No. 1 heavy melting scrap is

TABLE 19.—*Typical duty rates of iron and steel products (27)*

	TSUS No.	Rate of duty—1964	Statutory rate of duty
Iron and steel scrap.[1]	607.11	Free	Free.
Pig iron and cast iron.[2]	607.15	20 cents per ton	$1.125 per ton.
Spiegeleisen [2]	607.20	75 cents per ton	75 cents per ton.
Plates and sheets	608.84	8 percent ad valorem	20 percent ad valorem.
Structural steel	609.80	0.1 cent per pound	0.2 cents per pound.

[1] Duty temporarily suspended as provided by P.L. 88-324, effective July 1, 1964.
[2] May not contain more than: Chromium, 0.2 percent, molybdenum, 0.1 percent, tungsten, 0.3 percent, and vanadium, 0.1 percent.

TABLE 20.—*Duty added for amount of alloying element in iron products (26)*

	Rate of duty 1964	Statutory rate of duty
Over 0.2 percent by weight chromium.	1.5 cents per pound on chromium content in excess of 0.2 percent.	3 cents per pound on chromium content in excess of 0.2 percent.
Over 0.1 percent by weight molybdenum.	35 cents per pound on molybdenum content in excess of 0.1 percent.	65 cents per pound on molybdenum content in excess of 0.1 percent.
Over 0.3 percent by weight tungsten.	50 cents per pound on tungsten content in excess of 0.3 percent.	72 cents per pound on tungsten content in excess of 0.3 percent.
Over 0.1 percent by weight vanadium.	40 cents per pound on vanadium content in excess of 0.1 percent.	$1.00 per pound on vanadium content in excess of 0.1 percent.

TABLE 21.—*Composite price of No. 1 heavy-melting scrap, per long ton*

[Pittsburgh, Chicago, and Philadelphia]

Year	Composite price			Year	Composite price		
	High	Low	Average		High	Low	Average
1949	$41.36	$19.33	$27.56	1957	$59.37	$32.33	$46.75
1950	44.02	26.58	34.75	1958	43.10	32.73	38.08
1951	46.15	42.00	43.15	1959	45.67	34.41	40.49
1952	42.00	40.10	41.79	1960	41.83	28.33	32.95
1953	44.60	31.33	39.52	1961	39.42	31.50	36.28
1954	33.40	23.83	28.59	1962	37.41	23.58	28.23
1955	50.42	34.48	40.19	1963	28.67.	25.33	27.11
1956	64.59	45.08	53.82				

Source: Iron Age.

given in table 21. This illustrates the price fluctuations over a 15-year period.

The steel industry has averaged over $1 billion a year for the last 15 years in capital outlays for property additions, improvements, and acquisitions. Capital expenditures in the first years of this period were aimed primarily toward expanding the industry's production capabilities. However, in the past 5 or 6 years the shift has been toward increased productivity and the development of new and improved products. These expenditures have been divided between new plant construction or old plant modernization; between relining an open-hearth or constructing an oxygen converter; between rebuilding a bloom mill or starting continuous casting. This makes an estimate of cost-per-ton for this period of capital construction very difficult.

To illustrate for a specific year, 1963, 85 companies produced steel ingots and castings, employed an average of 520,000 people, and produced 109.3 million ingot tons of steel for which they received $14,453 million, with a net income of $782 million.

A summation of expenses involved in production are—

	Millions
Employment costs	$5,607
Products and services bought	6,174
Depreciation, depletion, and amortization	996
Taxes—Federal, state, and local	927
Interest	127

This means that the employment costs are 38.4 percent of total revenue, money expanded for products and services 42.3 percent, reserves for wear and exhaustion 6.8 percent, taxes 6.3 percent, and dividends 3 percent (*5*). Table 22 gives the components of this cost for 1954–63.

Capitalization as of December 31, 1963, was comprised of—

	Millions
Earned surplus	$6,887
Capital surplus	919
Preferred stock	640
Common stock	2,563
Total stock and surplus	11,009
Total long-term debt	2,689
Total capitalization	13,698

TABLE 22.—*Employment costs in steel industry*

[Millions]

Year	Wages and salaries	Social security and other employment benefits	Pensions	Total
1954–58 (average)	$4,329	$248	$221	$4,798
1959	4,578	325	237	5,140
1960	4,838	470	228	5,536
1961	4,673	466	213	5,352
1962	4,765	548	168	5,481
1963	4,841	585	181	5,607

Source: Annual Statistical Report, American Iron and Steel Institute.

TAXES

Federal taxes on the 1963 income of the iron and steel companies (representing 85 companies) was about $646 million, or 4.5 cents on each sales dollar.

Local, State, and miscellaneous taxes incurred by the iron and steel companies in 1963 were over $281 million.

The total of Federal, State, and local government taxes paid by these companies was over $927 million, exclusive of social security, and similar employee benefits, or 6.4 cents on each sales dollar.

TRANSPORTATION

The mode of transportation of iron and steel raw materials except coal, fluxes and refractories and iron and steel products is given in table 23. The iron and steel products moved by railroads include billets, blooms, ingots, bars, rods, slabs, nails, wire, woven wire, manufactured iron and steel products, and iron and steel products not classified. The iron and steel products moved by water include finished, semifinished, and rolled, iron and steel and pipe and castings. Data are not available on transportation of iron and steel products by truck.

The cost of transportation usually is less for raw materials than for finished products and therefore steel mills are located near markets.

TABLE 23.—*Transportation of raw material metallics for the iron and steel industry and iron and steel products in 1962*

[Thousand short tons]

	Railroad [1]	Water [2]
Iron ore	129,155	99,428
Iron and steel scrap	26,734	5,941
Pig iron	5,100	1,268
Ferroalloys	2,479	[3] 4,312
Iron and steel products	87,146	13,119
Total	250,614	124,068

[1] Freight Commodity Statistics, Class I railroads in the United States, Interstate Commerce Commission, Bureau of Transport Economics and Statistics, pp. 7–8. Total freight traffic (including duplications).

[2] Waterborne Commerce of the United States, Calendar Year 1962, Part 5, National Summaries. Department of the U.S. Army, Corps of Engineers, pp. 12–17. Includes imports, exports, lakewise, and internal waterways.

[3] Includes ferroalloy ores.

RESEARCH (10, 24)

The steel industry engages in fundamental or basic research in physics, chemistry, physical chemistry, thermodynamics, and all branches of metallurgy, and the industry also supports research in these subjects in private foundations and university laboratories. According to a survey report by the National Science Foundation, the industry expended $5 million per year for basic research in primary ferrous products 1957–59 inclusive, $8 million in 1960, and $7 million in 1961.

Applied research and development (R&D) in the steel industry is directed toward lowering production costs, conserving raw materials, im-

proving quality of existing products, and developing new products. The industry expended $60 million for R&D in primary ferrous products in 1959, $68 million in 1960, and $74 million in 1961. These figures, although developed by a comprehensive sample survey of industry, are believed to be low because the cost of research on fabricated metal products was not included. It is noteworthy that in November 1964, the United States Steel Corp. was continuing to introduce an average of two or more new or improved products every month. All the larger steel companies maintain research establishments that in setting, size, and appearance, resemble university campuses. Others maintain research laboratories commensurate with their scale of production, and even the smallest engages in some form of steel research. All this activity leads to the conclusion that current steel industry annual expenditures for R&D probably are as high as $150 to $175 million. Industry estimates placed the total at over $100 million in 1964, with an estimated 5,000 scientists, engineers, and supporting personnel working in research (*24*).

The Department of Defense and the Department of the Interior, through its Bureau of Mines, are responsible for essentially all the Government's research on iron and steel. Defense Department research is directed toward development of high-strength and high-temperature steels for service in armor, guns, aircraft, missiles, and other such military equipment. The work is done principally by contract with private industrial concerns, private foundations, and universities. Some Defense research has been done under cooperative agreements with the Bureau of Mines and other Government agencies. Department of Defense iron and steel research is typified by its maraging steel project in which the ultimate objective was to (1) determine the pertinent properties of maraging steels, (2) delineate the optimum techniques for processing and fabricating them, (3) define the important problems to be expected in using them, and (4) identify means to eliminate these problems.

The Bureau of Mines iron extractive metallurgical studies effectively cover the field from basic research through the first stages of applied research. It stops short of development except for small-scale constructing of research equipment. The Bureau operates an experimental blast furnace at Bruceton, Pa., for research, usually cooperatively with major steel companies. Research on the kinetics and mechanisms of iron oxide reduction and development of a mathematical model of a blast furnace are conducted at other Bureau laboratories. The Bureau's research on steel is on a very modest scale. It has to do principally with controlling fume, investigating the mechanisms of high-strength steels, and improving the quality of high-strength alloy steel ingots by adding rare earth alloys to melts during refining.

Steel research is so intermingled with and dependent on other work of the Department of Defense that it is not practical to calculate its cost. The Department's R&D expenditures have been at the rate of over $6 billion per year. A very small part of this was solely for iron and steel. Bureau of Mines expenditures for iron and steel research have been about $1.5 million annually since 1960.

OUTLOOK

Steel production should reach 137 million tons by 1975 and 150 million tons by 1980. This projection is based upon a growth rate for the steel industry at a rate slightly above that for the U.S. population through the balance of this century. Per capital steel consumption will now gradually increase because technical advances within the industry will make steel more attractive from an engineering, economic, and aesthetic viewpoint. The production figures for 1975 and 1980 are based upon a projected population increase using a 1.6 percent annual compound rate forecast by the Bureau of Mines. The growth factor derived from this population projection was modified because of the changes in steelmaking, improvements in steels, and the effect of competition furnished by other metals used as substitutes for steel.

Steel production has fluctuated during the last 20 years from extreme lows in 1946 and 1958 to extreme highs in 1955 and 1964. The average per capita consumption of steel based on ingot production for 1944–53 was 1,208 pounds, and for 1954–63 the average consumption rate was 1,160 pounds per capita. This shift to a lower consumption rate represents the fulfillment of the post World War II consumer demand, the inroads made by alternate materials and the better strength to weight ratio of improved steels.

By 1980, U.S. requirements for pig iron will be about 93 million tons and for scrap about 75 million tons. This projection is based upon the assumption that pig iron and scrap will remain basic ingredients in the furnace charge and that production from open-hearth furnaces will drop to about 40 percent of the total output of steel.

Basic oxygen converters will supply 45 percent of the total production with electric furnaces and others supplying 15 percent. Assuming that open-hearth furnaces will use about 59 percent pig iron (41 percent scrap), basic oxygen converters about 70 percent pig iron, and electric furnaces 100 percent scrap, an overall ratio of 45 percent scrap and 55 percent pig iron is expected to hold through 1980.

Further research on prereduced pellets may result in their use directly in steelmaking furnaces. Obsolescent ferrous scrap presents such a real disposal problem for the country that any changes in steelmaking will be modified to use scrap. For example, each junked automobile of those now littering the countryside could contribute about one ton of ferrous scrap. Five million cars per year are being scrapped now and, with this number steadily increasing, there will be a constant pressure on both industry and Government to utilize this scrap to keep the eyesore of auto junkyards at a minimum. Pressure casting and continuous casting techniques which will reduce the available scrap generated in integrated steel mills will increase use of purchased scrap. No new open-hearth furnaces will be built in the next decade, since steelmakers seem to be able to make all grades of steel in the basic oxygen converters satisfactorily, and the lower capital cost and greater operating flexibility make the oxygen converters more attractive when open-hearth furnaces need replacing.

The attempt to integrate steelmaking from furnace through continuous casting to continuous rolling, all controlled by automation, is proceeding slowly. Improved steel quality will come from vacuum degassing installed in connection with continuous casting. Computer control will probably take over only as the art of steelmaking becomes the science of steelmaking.

The population shift westward into an area which traditionally has favored wood and concrete for construction will not affect per capita steel consumption significantly since higher strength, lighter weight steels apparently are supplanting the bulkier concrete in the crowded Western urban areas.

Although world steelmaking capacity is now increasing faster than world steel consumption, the imbalance will change with the emergence of the less developed countries in Africa, Asia, and Latin America. In the immediate future the amounts spent on modernization will increase productivity enough to help the U.S. steel industry regain some of its losses in the export market.

PROBLEMS

The principal problem of the steel industry is to meet foreign competition and thus stem its increasing loss of position in domestic and world markets. The problem resulted from countries of Western Europe and the Japanese completely rebuilding their steel industries after World War II, incorporating technical innovations that enabled them to produce better steel at less cost. Meeting foreign competition leads to many other problems in reducing production costs and maintaining quality.

Cost problems result because accelerated steelmaking also speeds up equipment depreciation, necessitating either excessive repair or premature replacement. Also the short life of refractories in oxygen furnaces and the decreased number of heats between furnace relining needs much study.

Another problem in production is the need for retraining labor in the use of new machinery and automation devices which are installed to increase productivity.

There is also increased need for control of exhaust gases from the new accelerated steelmaking techniques, which are responsible for air pollution in the metropolitan areas.

Customer demand for products finished under more rigid specifications presents a continuing quality problem. Ways must be found to use the poorer grades of limestone and coal, which in many instances are all that is available after depletion of the high-grade.

Steelmakers have a quality problem in that scrap is furnished by independent dealers and processors, some of whom do not supply material that meets purity requirements. Use of obsolescent scrap is also a problem because there is a lack of data on its supply and movement, and there is no satisfactory method for analyzing it in bulk.

The need for faster, more sensitive analyses is a growing problem as the industry becomes more and more automated.

Another barrier to improved production and quality is the need for better understanding of the chemistry and physical chemistry of steelmaking and for more thermodynamic data with which to control the makeup of charges and operation of steelmaking furnaces.

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STONE

By Perry G. Cotter [1]

STONE generally means rock fragments or blocks removed from their original environment for use in construction or industry. Production of dimension stone for buildings, memorials, and other structures demands methods which are essentially different from those used to produce crushed stone. Uses are also fundamentally different, and therefore the branches of the stone industry must be viewed differently. For the preceding reasons the stone chapter consists of three sections: Dimension stone (except slate), slate, and crushed and broken stone.

DIMENSION STONE (EXCEPT SLATE)

Dimension stone competes at a disadvantage with an ever-increasing variety of other building materials, largely because it is costly to mine, prepare, transport, and install and because of the modern trend to construct buildings having a much shorter life expectancy than was customary 50 years ago. However, there is a renewed recognition of stone's unique properties for ornamentation and for protection against the weather, and demand for many varieties is rising. The principal varieties of stone—marble, granite, limestone, and sandstone—are used mainly for buildings and memorials, but substantial quantities are still produced for curbings, flagging, and miscellaneous uses.

The durability, strength, color, and density have important bearings on the value of stone for building and ornamental uses, but public preference is changeable and stones which are greatly in demand may lose their markets almost overnight.

The outlook for the memorial stone industry is only fair because more and more cemeteries are forbidding installation of grave stones, but stone for construction should continue to maintain a slow rate of growth in production.

Problems of the industry are need for improvement of quarrying and machining operations, utilization of waste, and development of means for lowering final costs of stone put in place.

BACKGROUND

Size and Organization of the Industry

At the beginning of the 20th century, dimension stone was produced in much greater tonnage than crushed stone, but in 1963 dimension stone production accounted for only about 0.4 percent of the total quantity. Nevertheless, there are about 700 active plants and value of sales exceeds $96 million annually in 45 States.

Quarrying and dressing blocks of stone may well be the most ancient of the mining industries. In the United States use of stone for construction began with the earliest settlements and production attained its zenith many years ago. Decreasing demand, however, began in the early 1890's, caused by development of steel skeleton construction and the rising use of concrete. Reinforced concrete, in fact, became an essential part of the skeleton structure, but that was only one of its many structural uses. Concrete, a stone-like material that can be poured in place, or can be cast or molded into any desired shape, has such decided advantages over stone, both in cost and convenience, that over half a century ago it began to replace stone extensively. Stone, however, is still preferred for its attractive appearance in many structures.

Other branches of the dimension stone industry besides building construction also suffered from competition with concrete. It has taken

[1] Commodity specialist.

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the place of flagstones in sidewalk construction, and it has extensively displaced curbstones and paving stones on city streets. This reduced market has posed many problems for stone producers.

Dimension stone producers may be divided into three main categories, based upon plant operations. The first group quarries stone and sells it as rough blocks or slabs; the second quarries stone and also uses it in manufacturing finished products; and the third group only buys sawed slabs or rough blocks of stone and manufactures a finished product. Bureau of Mines production data are compiled on the basis of quantities and values of sales of both rough blocks and finished products by primary producers.

Geographic Distribution of the Industry

The Appalachian Mountains extending from Maine and Vermont to Georgia and Alabama form a region in which igneous and metamorphic rocks abound. Important deposits of granite and marble have been developed in this territory. The extensive middle western area lying between the Appalachian belt and the Rocky Mountains is characterized by nearly horizontal sediments such as the famous limestone deposits of Indiana, and the well-known sandstones of Ohio. Commercially important granite deposits also occur in this area, notably in Minnesota, South Dakota, Wisconsin, Missouri, Oklahoma, and Texas.

In the Rocky Mountain belt numerous igneous and metamorphic rocks occur, and from this belt westward to the Pacific coast, igneous rocks prevail. Limestones, which occur, though not as abundantly as in the East, have in places been metamorphosed into marbles. Volcanism of comparatively recent geologic age has produced lavas, rhyolites, and volcanic tuffs that rarely occur in the Eastern or Central States. Sandstones suitable for commercial use occur in widely distributed deposits in nearly every State. About half the States are currently producing sandstone.

Building and ornamental stones are plentiful in many sections of the world. The marbles of Africa, Italy, France, Spain, Belgium, and England; the granites of Scotland, Finland, Norway, and Sweden; the granites and marbles of Canada; the travertine of Italy; and the onyx marble of Mexico.

Definition of Terms, Grades, and Specifications

Naturally occurring rock material cut, shaped, or selected for use in blocks, slabs, sheets, or other construction units of specified shapes or sizes, used for external or interior parts of buildings, foundations, curbing, paving, flagging, bridges, revetments, or for other architectural or engineering purposes is termed *dimension stone*. This term is also applied to quarry blocks from which pieces of fixed dimension may be cut (*3*).[2] Aggregates combined with cement to form building units, terrazzo granules, facing granules, and reconstituted or synthetic marbles and granites are not considered dimension stone. Marble, granite, limestone, and sandstone provide the bulk of dimension stone, although slate, diorite, basalt, diabase, and others are used locally or for specific purposes. *Marble* denotes a metamorphic rock composed essentially of calcite, dolomite, or a combination of the two, but long usage of the term by the quarry industry also includes serpentines, alabaster, onyx, travertines, and some granites. *Granites* are essentially fine to coarse-grained rocks of igneous origin with quartz and feldspar as the major components and as accessory minerals the various micas, pyroxenes, and olivine. A German definition limits the term granite to one composed essentially of quartz with equal parts of biotite and muscovite mica, but quarrymen customarily include with the granites, quartz-diorites, syenites, quartz-porphyries. Gabbros, schists, and gneisses. *Limestone* is a sedimentary rock composed of calcium carbonate. Usage includes under this term dolomitic limestone or dolostone, oolitic limestone, and crystalline limestone. Some highly crystallized limestones can be polished and are properly termed marbles. *Sandstones* are composed of quartz grains cemented with calcium carbonate, iron oxide, clay, feldspar, or silica. *Quartzites* are composed of silica grains so firmly cemented by silica that fracture occurs through the grains rather than around them. The term *freestone* although commonly understood to refer to a free-splitting sandstone is somewhat ambiguous and is also applied to a number of other sedimentary rocks. In addition to stone cut or shaped according to architects or builders specifications, the Building Stone Institute defines a number

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

of other units (*8*). Rectangular blocks having sawed, planed, or rock-faced surfaces are termed *ashlar*. Rough, irregular pieces of broken stone, partly trimmed, squared, or irregular are called *rubble*. Large irregularly shaped stones, used for facing bridge abutments and breakwaters, are termed *riprap*.

Because stone is a natural product, blocks from various quarries, and even from different ledges within the same quarry, vary greatly in texture, color, and durability, and for that reason architects and builders desire freedom in selection. Therefore, architectural specifications relate primarily to workmanship and surface finish, and engineering specifications are concerned with strength and durability. The stone is usually selected by the purchaser from samples and brochures furnished by the producer, and with due consideration given to the reputation of the stone and dealer. For massive buildings the ability of the quarryman to furnish large tonnages of stone having uniform color, texture, and soundness is fundamental.

The desirable properties of dimension stone, in addition to those relating to workability and the tests that measure it, depend upon whether the stone is to be used for interior or exterior work. For interior use, desirable properties include attractive color and texture, reasonable strength, and resistance to abrasion and cleaning solutions. Exterior building stones, if ornamental facing veneers are excepted, may be less attractive in color than those used for interior trim, but must have greater resistance to daily and seasonal changes in temperature, freezing of water, and atmospheric contaminants.

Long-term use of either interior or exterior stone, under a variety of environmental conditions, indicates durability under similar conditions, and may show its suitability for a particular purpose. However, conditions are subject to change, for example, when coal replaced wood for heating and industrial uses many European cathedrals deteriorated rapidly. Furthermore, the application of the time test alone may prevent many good stones from being considered as construction material. In order to forecast the probable behavior of new stone, the National Bureau of Standards and others have conducted research and devised tests to determine resistance to abrasion, fire, atmospheric acids, and solubility in water, as well as methods to determine the physical properties of strength, porosity, toughness, elasticity, and density (*5–7*). The American Society for Testing and Materials Committee C–18, Natural Building Stone, is presently engaged in developing specifications and test methods for a wide variety of dimension stones.

Specifications have been established for stone used in Federal buildings and are itemized in a 13 page pamphlet entitled Stone Work, issued by General Services Administration, Public Buildings Service, May 1955. The specifications indicate the physical and chemical properties required and cover the dimensions, design, surface finish, workmanship, and methods for setting.

For non-government construction architects or builders may prepare specifications, but more often they are guided by specifications prepared by the various building stone institutes or associations with such modifications as may be mutually agreed upon.

Monumental stone specifications, particularly for Federal cemeteries, are most exacting, and only stone of highest quality is used. The stone must be free from such flaws as cracks, hairlines, iron spots, and other blemishes. Texture and color must be pleasing, and the stone must usually be able to take and maintain a high polish with good contrast between polished and hammered surfaces. The arrises, developed in carving, must be sharp and free from any tendency to crumble. Demands for color and style in memorial stone are continually changing factors. For these reasons waste in production of memorial stone may amount to as much as 85 percent.

Technology

Geology

Among the geological features of a rock that are significant in its use as a dimension stone are jointing, sedimentary stratification, and secondary cleavage. Nearly all rocks are jointed. The joints may be open and conspicuous or closed and almost imperceptible. Closed or incipient joints cause planes of weakness known variously as rift or gain which largely determine the shapes of the blocks which may be extracted from a quarry. Where properly distributed they may facilitate quarrying; in other cases they may prohibit extraction of large-sized blocks. Some rocks of otherwise good qualities are so cut by joints that they are useless for anything but crushed stone. The bedding planes of sedimentary rocks also influence the utility of stone and like joints may be useful or disadvantageous. The secondary cleavage of some rocks enables them to be split into uniform slabs.

The durability of a rock depends in part on its perviousness to water, which may enter along bedding planes, fracture planes, or through minute pore spaces between the mineral particles. The water may cause chemical changes

or by freezing and thawing cause the rock to weaken and disintegrate. For this reason the less pervious rocks usually have greater durabilty.

As minerals resist weathering to different degrees, the mineral composition of a rock is a factor in determining its durability. Abundant mica, especially where segregated along the stratification planes, permits easy splitting of the rock; it may weather more quickly than surrounding minerals giving a pitted appearance. Flint or chert in abundance is deleterious to limestones and marbles because, being more resistant, it stands out in relief on weathered surfaces, interferes with smooth cutting and polishing, and often causes the rock to splint along the lines of the flint inclusions.

Mining and Milling

Methods for quarrying dimension stone vary according to the type of rock, depth of the deposits, and ultimate use. The damaging effect of explosives on dimension stone has been recognized for many years, and blasting is avoided wherever possible. The usual procedures followed are to cut the stone from the quarry face into large blocks with channeling machines or wire saws, undercut the stone at floor level, break the stone free by wedging, and turn the stone down on piles of rubble or old tires by use of a derrick. The mass of stone is then cut into blocks of the desired size by drilling and wedging, and the blocks are hoisted from the quarry by stifleg derricks. Common limestone mill block sizes are 10 by 4 by 3 feet and 10 by 4 by 4 feet.

To obtain primary separation from ledges, most quarriers of granite and structural sandstone prefer drilling and broaching. Deep holes are drilled close together in a straight line, usually with detachable tungsten carbide bits and hollow drill steel, and the partitions between the drill holes are removed with broaching tools. The most modern method for cutting out granite blocks utilizes an oxygen-kerosine jet flame, but many quarries make the primary cuts with the wire saw. Wire sawing equipment consists of one- and three-strand wire cables, up to 16,000 feet long, running over pulleys as a belt. When fed by a slurry of sand and water, and held against the rock by tension, it cuts by abrasion. The wire saw conserves power, labor, and stone (*2*).

Quarrying marble, limestone, and softer sandstone is usually accomplished by the use of electrically powered channeling machines that operate by a chopping action upon three to five steel chisels, similar to that of a reciprocating drill. As the machine travels back and forth upon a track it makes channels about 2 inches wide and 4 feet apart. After the cut is made blocks are separated at the quarry floor by wedging, and further divisions are made by plug and feather splitting (*1*).

In the mill dimension stone blocks are cut to predetermined shapes as specified by the contract. The various machines for sawing, planing, jointing, grinding, turning, and fluting have a resemblence to those used in the wood working industry, except that the saws are set with diamond teeth and the other operations utilize silicon carbide grinding wheels. Pneumatic hoists and wheeled conveyors now minimize the amount of physical labor required. Carving operations require the most skill. Large statues are carved using pneumatic hand tools, with reference to plaster models, but smaller repetitive designs are frequently carved free hand by operators who have long experience. Designs and inscriptions for memorial stones are cut from drawings on plastic sheets. The sheets are then cemented on the previously polished stone and sand or shot blasting cuts the design into the sections of the stone not protected by the plastic sheet.

The quarrying and milling of dimension stone have been covered in detail in Bureau of Mines publications. Later information is given in "The Stone Industries" (*2*), and in "Industrial Minerals and Rocks" (*1*).

Uses

Dimension stone is used as building stone, monumental stone, paving stone, curbing, and flagging.

Although with the advent of steel and concrete construction, the dominant position of dimension stone for load-bearing structural uses declined, the industry has adapted to the changes, and emphasis is now placed on the economical production of thin slabs of veneer for both interior and exterior application. Furthermore, although granite and marble continue to be held in highest regard for facings because they are colorful and can take and retain a high polish, the more drab limestones and sandstones are now produced with many varieties of textured surfaces which are attractive to architects and are in increasing demand.

Memorial stones have the highest unit value. Included under this category are tombstones, statuaries, and grave markers. Mausoleums, sarcophagi, and commemorative memorials are fundamentally structural units, and although the quality of stone entering into their construction is similar in grade to monumental stone, in other aspects they are dissimilar.

Flagstones are used around small commercial buildings and residences for decoration, utility, and lawn protection.

The use of surface plates for high-precision measurements in machine shops and instrument work has become standard practice. These plates are made from granitic or basaltic rock of various types, although the generic name is *black granite*, and are extremely hard, nonwarping, rust-and-corrosion proof, and dimension changes are slight under variations in temperature.

Byproducts and Alternate Materials

Byproducts consist of quarry blocks, which have been rejected because of structural flaws or blemishes, and spalls or fines produced during trimming or shaping operations. Rejected blocks are sometimes used for breakwaters and revetments, and other waste material is used for riprap and roadstone. Waste marble and limestone is often burned for lime or ground and used for whiting and as mineral fillers.

Waste, which in many places amounts to 80 or 90 percent of quarry production, is an ever-present problem for producers, and in some areas the piles of waste accumulated during the years cover valuable deposits of dimension stone and make recovery costly.

Building stone has been replaced to a large extent by concrete, glass, brick, stainless steel, aluminum, porcelain enameled steel, and plastics. The put in place cost of many of these alternate materials is lower than that of stone, but stone is still preferred for the more dignified buildings where its architectural adaptability, permanence, and prestige are of prime importance.

Reserves

Although rock formations suitable for dimension stone are numerous, those having the requisite qualities that can be commercially exploited are commonly confined to restricted areas. Nevertheless, in the major producing districts the reserves are apparently adequate for many years' operation. No definite reserve figures are available.

Sources of Statistical Information

Statistical data of the industry are obtained from the individual producers and compiled annually by the Bureau of Mines. As Bureau figures are based on actual sales of quarry products, these products are recorded at the point where they first enter trade. If the quarryman sells stone in rough blocks, his sales are so recorded. If he owns a processing plant and fabricates the rough blocks into finished building stone, the sales of the finished products are recorded. Part of the Bureau's data pertain to the rough-block stage of preparation and part of them to the finished-product stage. Hence the total value of production indicated by Bureau figures represents a combination of the two stages.

Substantial quantities of stone enter foreign trade. Import and export data are compiled from records of the U.S. Department of Commerce.

Production, Consumption, and Trade

Although unique types of dimension stone, or those used for special purposes may be shipped appreciable distances, the usual marketing areas are restricted because of the relatively high cost of transportation, packaging, and handling. Production and consumption of dimension stone are virtually synonymous, although stocks of blanks for memorial stones are maintained by both producers and dealers.

Building and ornamental stones, both quarry blocks and finished stones, are imported in substantial quantities by domestic quarrymen and by importers. Imports are valued at about $20 million per year. Most of the imports consist of marbles from Italy, Spain, France, Greece, Portugal, Belgium-Luxembourg, and Mexico. Exports of building stone, chiefly to Canada, are approximately $1.6 million per year. Granite and other igneous rocks are imported from Finland, Sweden, and Canada. Travertine is imported from Italy, and onyx marble from Mexico.

Tariff regulations on stone are very complex because they involve many varieties, several stages of manufacture for each variety, and tariff changes from time to time. Tariff information on dimension stone can be found in the Dimension Stone section of "Industrial Minerals and Rocks" (1).

Prices

Compared with other building materials, prices of stone are relatively high because stone is difficult to work and requires many hand operations. Also, because of its high unit weight, transportation expense adds substantially to the delivered cost. Price increases of stone in the past decade have not advanced out of proportion with those of other materials.

Transportation

Because of the weight, bulkiness, and handling difficulties of the product, transportation expense adds greatly to the unit delivered cost. Freight is an important factor in competitive marketing, although stone is commonly shipped long distances to satisfy special architectural demands.

TABLE 1.—*Dimension stone sold or used by producers in the United States, by kinds*

[Thousand short tons and thousand dollars]

Kind of stone	Quantity	Value	Quantity	Value	Quantity	Value
	1954–58 (average)		1959		1960	
Granite	591	$24,944	654	$26,588	600	$28,773
Basalt	73	391	14	377	14	365
Marble	118	12,838	137	18,085	129	17,743
Limestone	1,064	20,977	952	20,693	860	17,140
Sandstone	515	11,954	475	11,745	439	11,541
Slate	129	6,557	119	6,365	119	6,319
Miscellaneous	75	3,026	93	3,718	96	4,128
Total [1]	2,565	80,687	2,442	87,571	2,257	86,009
	1961		1962		1963	
Granite	662	$30,569	902	$32,012	753	$32,796
Basalt	13	465	103	649	93	620
Marble	157	18,566	146	18,739	150	21,002
Limestone	855	16,738	896	16,847	895	18,134
Sandstone	391	11,134	390	10,904	412	11,443
Slate	124	6,749	151	7,441	153	8,055
Miscellaneous	113	3,872	141	4,095	160	4,268
Total [1]	2,315	88,093	2,729	90,687	2,016	96,318

[1] Figures may not add to totals owing to rounding.

TABLE 2.—*Dimension stone sold or used by producers in the United States, by uses*

[Thousand short tons and thousand dollars]

Year	Short tons	Value	Short tons	Value	Short tons	Value
	Building		Rubble		Roofing (slate)	
1954–58 (average)	1,562	$49,342	378	$1,319	39	$2,316
1959	1,443	55,998	360	1,606	29	1,810
1960	1,316	52,953	330	1,743	25	1,611
1961	1,240	54,767	424	2,143	31	1,796
1962	1,320	55,133	537	2,022	30	1,767
1963	1,332	55,680	620	2,687	32	1,965
	Millstock (slate)		Monumental		Paving blocks	
1954–58 (average)	21	$2,916	237	$17,849	24	$158
1959	21	3,110	236	17,862	29	144
1960	23	3,053	221	19,254	31	131
1961	26	3,202	226	18,770	76	295
1962	30	3,529	227	19,246	264	937
1963	30	3,825	277	24,099	4	86
	Curbing		Flagging		Total [1]	
1954–58 (average)	124	$3,509	180	$3,278	2,565	$80,687
1959	155	3,811	169	3,230	2,442	87,571
1960	157	3,929	154	3,335	2,257	86,009
1961	149	3,859	143	3,261	2,315	88,093
1962	155	4,236	166	3,817	2,729	90,687
1963	153	4,026	168	3,950	2,616	96,318

[1] Figures may not add to totals owing to rounding.

Research

Research by the dimension stone industry and manufacturers of machinery has resulted in improvements in methods for extracting and shaping stone. Installed costs have been reduced by the development of modular units and precast sections, and a wide variety of surface finishes have been made available. The larger companies have conducted research on increasing durability of their products, adaptability of stone for interior and exterior work, and color stability. Associations of memorial stone producers have conducted marketing research programs designed to improve the quality of stone offered to the public and to increase the dependability of dealers. Diamond set gang saws, capable of cutting 40 or more sections of veneer stone at once, have resulted from industrial research.

A few educational institutions have conducted research on dimension stone, particularly on the problems of utilizing waste products. The National Bureau of Standards has conducted research on the physical and chemical properties of stone, its durability and on development of test methods by which various stones can be evaluated (*5–6*).

TABLE 3.—*Annual average value of dimension stone in the United States*

[Per cubic foot]

Year	Building stone (dressed)				Memorial stone (rough and dressed)	
	Granite	Marble	Limestone	Sandstone	Granite	Marble
1954–58 (average)	$7.62	$10.18	$2.62	$2.67	$5.61	$11.80
1959	9.20	12.20	2.69	2.97	5.67	16.56
1960	10.23	12.49	2.57	3.10	6.52	17.25
1961	11.25	11.78	2.73	3.69	6.19	16.14
1962	12.18	12.82	2.92	3.48	6.31	15.32
1963	10.55	13.03	2.89	3.40	5.88	14.92

OUTLOOK

It appears unlikely that the dimension stone industry will, in the near future, approach the production volume of the pre-World War II era. Three factors limit production: (1) increasing demand by builders for more efficient structures with greater rental or usable space—obtained by functional design, modular construction units, and elimination of dimension stone as a load-bearing material—and with esthetic values gained through use of horizontal and vertical lines rather than the heavy columns and monolithic carvings common some years ago; (2) continuing competition from alternate building materials such as glass, metals, ceramic tiles, plastic panels, and precast concrete panels faced with exposed aggregate, colored glass, or mosaic tile; and (3) continuing growth of memorial parks and similar types of cemeteries which restrict or prohibit use of monuments and private mausoleums, thereby adversely affecting the segment of the dimension stone industry that produces monumental stone.

More favorable trends are seen in the growing use of dimension stone panels and veneers as independent units of construction to protect interiors of buildings from the weather and to give attractive exteriors. New efficiencies in cutting thinner stone slabs, combined with the development of insulating panels faced with ornamental stone veneers, should also increase demand for dimension stone. The increased use of crushed and graded stone for exposed aggregate panels should enable dimension stone quarries to dispose of some waste material at a profit. Improved methods for attaching panels to structures make this sector of the industry more competitive by lowering labor costs.

PROBLEMS

Specifications and standard tests by which durability of stone may be forecast are either unavailable or not generally accepted as valid. There appears to be no significant correlation between compressive strength tests and durability, either in surface behavior (architectural appearance) or bulk behavior (engineering use). Present accelerated weathering tests based on resistance to freezing and crystallization tests such as the sodium sulfate soak are unreliable. The standard Los Angeles and Deval tests give insufficient information for rating building stone.

Present methods of producing dimension stone yield a high percentage of waste which can be disposed of only on a highly competitive market after costly additional processing.

The lack of dimensional standardization increases cost of many building stone units. Costs remain high and broad use of dimension stone is restricted because mechanization of stone processing plants and development of methods for quantity production have lagged.

Lack of uniform terminology causes confusion among producers, builders, and architects.

Spalling, discoloration, and fracturing of stone after it is in place are continuing sources of concern and tend to lessen confidence in durability of some stones.

The industry, in general, lacks complete knowledge of many modern materials that may be used to seal porous stone for protection against weathering and decay.

The principles involved in cleaning stone buildings, and the deleterious effects of some techniques now in general use, have received insufficient consideration.

Continuing problems are those relating to increasing efficiency of drilling, blasting, sawing, shaping, finishing, and handling stone.

SLATE

Slates are argillaceous rocks of sedimentary origin which have the common property of splitting readily in thin plates.

Because of increased competition from a wide variety of lower priced substitutes, markets for most uses of slate have been declining for many years.

Utilization of the enormous dumps of waste slate and increased efficiency in production methods are vital to the industry.

BACKGROUND

Size, Organization, and Geographic Distribution of the Industry

In 1963 there were 49 slate quarry operations in the United States. There are two branches of the industry which are not only virtually independent of each other, but are to some extent competitive. One branch comprises the preparation of roofing slates and millstock of various kinds. The other prepares slate granules used on composition roofing, slate flour for fillers, and lightweight aggregate. Total sales of the two branches are about $11 million per year.

The slate industry is centered in four principal locations: Lehigh and Northampton Counties, Pa., near Bangor, Pen Argyl, Windgap, and Slatington, Pa.; Monson, Maine; New York-Vermont area near Granville, N.Y., and Poultney, Vt.; and Buckingham County, Va.

Slate has also been produced on a small scale in Arizona, Arkansas, California, Georgia, Michigan, Tennessee, and Utah.

Definition of Terms, Grades, and Specifications

Slate is a fine-grained metamorphic rock that has a more or less natural cleavage, which permits it to be split readily into thin smooth sheets. The most common slates are dark gray to black, owing to carbonaceous material present in the original muds, but other varieties may be light gray, red, green, or purple. The average slate contains over 50 percent silica, 15 to 20 percent alumina, and smaller amounts of iron (hematite, pyrite, or magnetite), carbon, sulfur, and other elements.

Electrical slate is principally of the mica variety and should have high mechanical and dielectric strength, be readily machinable, and have low porosity. Structural slate, used for sanitary purposes, laundry tubs and sinks, must also have a low porosity, and for floor tile, steps, and flagging a high transverse strength is required. Blackboard slate specifications usually require that the material be free from blemishes or other imperfections. Roofing slate is sold in squares. A *square* is a sufficient number of any size to lay 100 square feet of roof, allowing the standard 3-inch lap. The estimated weight of a square of ¼-inch slate is 1,000 pounds.

Strength, porosity, bulk density, color fastness, resistance to weathering, and cleavage are the factors which determine suitability of slate for roofing.

The standard Federal specification for roofing slate is designated Slate; Roofing, SS–S–451, dated July 26, 1932.

The term *ribbons* applies to wavy or banded structures that appear in certain slates, notably those in Virginia and Pennsylvania.

The term *millstock* includes all forms of structural slate used in exterior or interior construction.

Technology

Geology

Slates were originally deposited in shallow water as fine, even-grained muds composed of very fine particles of clay. The early layers were compacted into a dense, bedded rock by the weight of accumulated sediments, and eventually heat and pressures induced by earth movements, developed in the beds a tendency to part along even planes. It is this property which is termed "slate cleavage" (*1*). During this process of metamorphism certain chemical changes occurred in the particles, which composed the original clay, and these changes also assisted in the development of parting planes by orienting the particles in positions normal to the direction of pressure.

Mining and Milling

Slate is usually obtained from open quarries. In Pennsylvania where the beds are nearly vertical and the slaty cleavage dips 5° to 15° from horizontal, the quarries are deep and relatively narrow. A maximum depth of 700 feet has been attained and depths up to 450 feet are not uncommon. Open bed planes known as loose ribbons commonly make quarry walls. In the absence of loose ribbons quarry walls are maintained as far as possible parallel with, and at right angles to major joints. In the New York-Vermont area where slaty cleavage dips at angles of 40° to 50°, quarries are wider and shallower. In Virginia where the slaty cleavage is almost vertical the quarries are deep and wide. In Maine where the major commercial slate bed is narrow and nearly vertical, underground shaft mining is followed.

Primary cuts in the Pennsylvania quarries were made originally with channeling machines which travel back and forth on a track and cut a channel with reciprocating chisel-like bars. In 1926 the Bureau of Mines assisted the industry in introducing the wire saw. When fed with a slurry of sand and water, and held by tension against the rock, it cuts by abrasion. This equipment replaced channeling machines in the Pennsylvania slate region, but it has not

been adopted in other slate-quarrying centers. In the New York-Vermont area and in Buckingham County, Va., primary breaks are made with small charges of explosives in drill holes, advantage being taken wherever possible of open joints and bed seams.

Experiments are being made by the industry in the use of diamond circular saws for making primary cuts in quarries, but no definite results are yet available.

At quarries where roofing slate is made, the quarry blocks are subdivided by drilling and wedging parallel to the slaty cleavage and rift, which is a second direction of splitting less pronounced than slaty cleavage and usually at right angles to it. In the third direction at right angles to both slaty cleavage and rift there is no tendency to split. It is known as the hard way and designated locally as the *sculp*. The slabs of slate split on cleavage and rift to the desired dimensions are usually broken by sledging in the sculp direction, but sometimes they are cut to length with circular saws. The splitters take the blocks that have been reduced to the thickness of eight slates, and split them into roofing shingles with a thin chisel and mallet, always splitting in the center of each block and subdivision thereof. The trimmer takes the shingle from the splitter and trims it to the largest commercial size obtainable. A common trimming machine has a straight blade operating like a paper cutter.

Blackboards, electrical panels, table tops, sinks, and all types of structural slate products such as steps, baseboard, and window sills are made in mills usually equipped with overhead traveling cranes of about 5-ton carrying capacity. Quarry blocks brought to the mill are first measured and marked according to the sizes required for the uses for which they are best adapted. They are then placed on saw beds and cut to size. Saws range from 24 to 48 inches in diameter and make cuts about ⅜-inch wide.

Uses

For generations, both in Europe and the United States, virtually the only use for slate was for roofing. Some slate roofs built in the eighth century are still compact and weather resistant. If the cost of slate roofing could be brought within the range of other types of roofing many people would prefer it to tiles, asphalt shingles, and asbestos shingles. Deterrents to greater use of slate roofing, in addition to the prime cost, are cost of installation, and the extra strong framing and roof trusses required for support. Millstock is used in exterior or interior construction as veneer, mantels, lavatory slabs, electrical panels, laundry tubs, billiard table tops, grave vaults, and blackboards.

Byproducts and Alternate Materials

Waste slate when ground to a fine powder is used as a filler in putties, linoleum, wallboard, abrasives, polishes, ceramic ware, and paints. Slate, crushed and screened to obtain minus 8-mesh, plus 35-mesh particles, is used for roofing granules. Small amounts of waste slate are bloated at a temperature of approximately 2,000° F to form lightweight aggregate.

Slate has to meet competition from many sources. As a roofing material, alternates such as sheet metal, wood shingles, asbestos-cement shingles, tiles, rolled roofing, and built-up roofing are available. For blackboards it competes with colored glass, porcelain enameled steel, and special painted surfaces. For electrical panels, marble, soapstone, and plastics are in competition, and for other structural uses, marble, granite, limestone, sandstone, and concrete products are readily available.

Even the waste products, such as slate flour and expanded slate, must meet competition from ground marble, silica, limestone, and expanded shales and clays.

Reserves

No systematic exploration of slate deposits has been made in the United States. From the geology of the Pennsylvania formations, as described by Behre, the deposits of commercial slate are evidently extensive enough to maintain the industry at current rate of production for many years. The resources in New York, Vermont, Maine, and Virginia are also extensive, although unmeasured.

Sources of Statistical Information

Statistics of the domestic slate industry are compiled annually by the Bureau of Mines. Data on imports and exports are assembled by the Bureau from figures compiled by the Department of Commerce. Foreign statistics are available for some countries, notably Great Britain.

Production and Consumption

Production and consumption of slate are virtually synonymous as stocks are moderate and more or less constant. The domestic industry has adequate facilities to supply all demands for slate, although temporary shortages may develop at times for certain types due to

unforeseen demands, for example, an abnormal call for roofing slate after a hurricane. Slate is predominantly a peacetime industry. Wars tend to depress rather than stimulate production.

Statistical data on slate can be found in the dimension and crushed stone tables of this chapter.

Prices

The average reported price for slate roofing squares, in 1963 was $24.26, approximately the same as in 1958. Millstock prices increased from 89 cents per square foot in 1962 to 95 cents in 1963. Flagstone prices, because of competition from many small local producers, remained about the same; 13 cents per square foot. Granules (including crushed slate for lightweight aggregates) declined in average value from $11 per ton in 1958, to $4.42 in 1963.

Research

Continuing research on production methods and utilization of waste is conducted by the College of Mineral Industries, Pennsylvania State University. Results of research are published as phases of the program are completed (*10–13*).

Research was conducted by the Bureau of Mines in conjunction with the industry and the National Slate Association beginning in 1926 and individual tests on bloating abilities of slate are made at the Bureau of Mines, Norris Metallurgy Research Laboratory, Norris, Tenn. Results of other research are described in Bureau of Mines Technical Paper 469.

OUTLOOK

Indications are that production of dimension slate will continue at the same low level that has been maintained for the past 5 years. For most uses of slate alternate materials are available at lower prices. Moderate increases may be expected in slate production used for lightweight aggregate and for mineral fillers. The expected increase in construction of schoolrooms, which could expand demand for slate blackboards, has been delayed because of reluctance of many communities to vote bond issues. Some increase is expected in demand for modular rubbed or riven slate veneer for curtain walls and interior flagging. This may offer an outlet for some types of slate that split unevenly.

PROBLEMS

Slate production is handicapped by falling demand and high production costs. Disposal of waste, approximately 90 percent of output, continues to be one of the most vital problems of the industry. Not only does this enormous proportion of waste increase cost of producing usable stone, but the huge waste dumps cover deposits which might be worked at a latter date.

Reluctance or financial inability of the industry to change from outmoded manufacturing methods and to adapt methods for winning and processing slate which have demonstrated their worth in other divisions of the stone trade tend to keep production of dimension slate a craft industry with accompanying high costs.

Again, higher labor costs, a direct result of lack of practical slate splitting devices, contribute to the decline of roofing slates, formerly the chief product of the industry.

CRUSHED AND BROKEN STONE

Crushed and broken stone, a basic construction, chemical, and metallurgical raw material, is a major commodity in both tonnage and value. Limestone is the most important rock, accounting for about 71 percent of the total crushed stone production. Large quantities of basalt, granite, and quartzite or sandstone also are used.

Accelerated highway and industrial construction are major factors in the increasing demand for crushed and broken stone. The bulk of stone production goes into construction projects; the remainder is used in cement manufacture and for chemical, metallurgical, and agricultural purposes.

The industry will continue to grow approximately at the same rate as the national population and economy. Its growth closely parallels trends in such basic economic indicators as gross national product, value of construction, and population.

Various types of this low-value commodity are produced in many sections of the country. Reserves are being depleted at a high rate, but adequate sources of supply remain although at progressively greater distances from consumption centers.

The competitive position of crushed stone in relation to sand, gravel, slag, and lightweight

aggregates makes cost control a major operating requisite. Quality control is also an important factor—rigid requirements have produced many different specifications for crushed stone for various purposes. Zoning regulations continue to be a serious factor because they handicap the utilization of deposits close to metropolitan areas and require the development of more distant deposits.

Other perennial problems relate to improving mining and beneficiation techniques, research on blasting practices to reduce damage from vibrations, transportation, and exploratory methods and equipment.

BACKGROUND

Although stone has been used as a building material since prehistoric times, the use of crushed stone has been greatly accelerated in recent years. A century ago Eli Whitney Blake's invention of a mechanical stone crusher gave impetus to volume production of crushed stone. Demand for macadamized roads began to increase slowly, but highway markets for crushed stone have developed within the last half century as a result of need generated by increasing use of rubber tired motor vehicles. Rigid and flexible pavement construction required machine-produced stone in ever increasing quantities. Rapidly, other markets for crushed stone also developed, such as portland cement, railroad ballasts, fluxstone, agricultural stone, and in the metallurgical and chemical industries.

At the turn of the century, sales of stone for road-building, railroad ballast, and concrete aggregate totaled about 25 million tons, but in 1963 it reached more than 451 million tons for these same purposes. Crushed stone in 1963 for all purposes totaled more than 685 million tons valued at $972 million at the point of production.

Size, Organization, and Geographic Distribution of the Industry

There are over 3,000 commercial crushed stone plants scattered over the Nation and the number and size have been increasing in recent years. The general trend has been toward an increase in the number of plants in the larger size groups and in a larger percentage of the total production by those groups. Plants producing over 900,000 tons annually account for about 3 percent of the total number of plants and about a fourth of the total tonnage. The 328 largest plants supply 51 percent of the commercial total. The portable plant is also becoming more important within the industry. Some plants produce stone for only one purpose such as roadstone or concrete aggregate. Others, particularly limestone producers, may market products meeting physical and chemical specifications for several diverse end uses.

In contrast with strictly commercial operations, numerous noncommercial operations are reported by States, counties, municipalities, and other government agencies as being operated by themselves or by contractors for consumption by these agencies. Noncommercial producers are on the increase owing mainly to the expanded highway program and the tendency for the contractor to maintain his own portable plant.

The industry exists in every State of the Nation. As one might expect, leading industrial States with large population report the largest production and use of the industry product.

Granite rocks, used for the production of mineral aggregates, are found in widely scattered sections of the country. Production of crushed granite is greatest in the mountainous Eastern and Western States, where granite terrains are common. Basalt, and similar igneous rocks, are quarried extensively in the Connecticut Valley, New Jersey, Pennsylvania, several sections of the Piedmont in the East, the Columbia Plateau, certain sections of the western ranges, and in Hawaii. Certain siliceous rocks, such as quartzites and sandstones, are quarried extensively in Arkansas, West Virginia, California, Pennsylvania, Texas, South Dakota, Wisconsin, and Minnesota; other desirable metamorphic materials are found in the Piedmont sections in the East and in many of the mountainous regions of the country. Limestone is the most important sedimentary rock used for crushed stone. It occurs extensively throughout the Valley and Ridge province of the East, throughout the Middle West, Kentucky, Tennessee, the Ozark Plateau widely scattered areas in the Great Plains and some small areas of the Far West. Marl, shell, slate, and marble are also crushed and used to some extent in a few States where local supplies are available.

Definition of Terms, Grades, and Specifications

The term *crushed and broken stone* is applied to irregular fragments of rock crushed or ground to smaller sizes after quarrying.

The terms traprock and granite are used in the broadest sense in the crushed stone industry. *Traprock* includes all dense, dark, and fine-

grained igneous rocks such as basalt, diabase, and gabbro. *Granite* includes the coarser grained igneous rocks such as true granite and syenite. Gneisses, although classified as metamorphic, are usually included with granite. *Quartzite* is normally considered a siliceous cemented sandstone which is indurated to the extent that when fractured it breaks across the grain. However, the term is sometimes applied in the industry to less indurated materials. Ordinarily a carbonate rock is classified as *marble* by the industry if it will take a polish although in the strict geologic sense it might be classified as a *limestone.*

Riprap consists of heavy irregular rock chunks used chiefly for river and harbor work, such as spillways at dams, shore protection, docks, and other similar construction that must resist the force of waves, tides, or strong currents. It is also used to fill in roadways and on embankments.

Terrazzo consists of small chips or pieces of stone, usually marble or limestone, about one-half to three-fourths inch in diameter, made by crushing and screening. Terrazzo chips are used with portland cement in making floors, which are smoothed down and polished after the cement has hardened.

Fluxing stone used in iron blast furnaces and foundries consists of pure limestone or sometimes dolomite. Usually material below 2 inches in diameter is eliminated. The most desirable size is between 4 and 6 inches.

True whiting is a finely divided calcium carbonate prepared by wet grinding and levigating natural chalk, a variety of limestone. *Whiting substitute* is a finely ground calcium carbonate, about 98 percent pure, contaminated by magnesia, silica, iron, or alumina, and should not be confused with chalk whiting or precipitated chalk.

Refractory stone consists of sandstone, quartzite, mica schist, soapstone, or other rock that will withstand a moderately high temperature without fusing, cracking, or disintegrating. It may be used in solid blocks or crushed and mixed with a binder to form bricks.

Stucco dash and exposed concrete facing consists of various types of stones, usually white or brilliantly colored, crushed to $\frac{1}{8}$- to $\frac{3}{8}$-inch size range.

Chicken grit is commonly composed of oystershell, limestone, and marble, although other materials, such as granite and feldspar, are sometimes used.

Agricultural stone is finely ground limestone used as an alternative to lime to neutralize or reduce acidity of soils.

Increasingly rigid requirements resulting through evolution of technical design have produced many different specifications for crushed stone. In the construction field alone, many volumes have been written on specifications, testing, and test methods by such organizations as the American Society for Testing Materials and American Association of State Highway Officials. In brief, the basic physical properties of aggregates, that affect their behavior when used for various structural purposes, include hardness, toughness, resistance to weathering, shape, size, cleavage, density, composition, porosity, structure, and color. Chemical and industrial applications usually require uniform and specific chemical composition with low limits on impurities.

Quality control of aggregates is concerned with the presence of reactive materials, organic matter, iron staining agents, soft and slabby particles, adhesion properties, porosity, grading, and durability. When the extent to which the aggregate influences the quality of the concrete was realized, aggregate specifications for the various construction uses were gradually established. Specifications were held within fairly rigid limits to insure that the end product met certain prescribed standards. Acceptance tests were based upon specified procedures such as those promulgated by the American Society for Testing and Materials (ASTM), American Association of State Highway Officials, and others. The ASTM specification for concrete aggregates (*15*) illustrates the type of provision commonly included in commercial specifications. The most common tests to determine whether a stone is suitable for use as construction aggregates are those for soundness, resistance to abrasion, specific gravity, particle shape and fracture, soft particles, and gradation.

Generally, construction engineers demand stone that is clean, strong, durable, sound, and dense. This is particularly true with respect to its use as coarse aggregate. Most engineers purchase their stone on specifications based largely on physical properties. Many of these specifications differ widely, particularly with respect to the exact application of the stone and to a lesser extent to the geographical location. The presence of alkalies, soluble sulfides, gypsum, and organic matter in the stone is objectionable to most users. Other important considerations are the individual size and particle size range of the stone. As a result, many types of rock are unacceptable for one or more construction uses since they are unable to meet the requirements.

Technology

Geology

Rock, as used in engineering geology, means a compact, semihard to hard, mass of naturally occurring material composed of one or more minerals. Rocks have been, and are presently being, formed in various ways; by cooling of molten rock, by disintegration of other rocks and subsequent recombination of the resulting minerals to form new rock types, by intense action of heat, fluids and/or pressure on preexisting rock types, by precipitation from water, by deposition of shells, and by condensation of a gas containing mineral particles.

Raw materials for the crushed stone industry comprise rocks of all three groups—igneous, metamorphic, and sedimentary—and from all periods of geologic time.

The geology of a region affects the crushed stone producer in three different ways through its influence on the topography, structure, and materials of a given area.

The topography of the area, which influences the drainage, the location of transportation routes, and accessibility for mining, is directly related to the geologic history of the area.

The underground structure determines the accessibility of industrially valuable stone, the exploitation and mining methods that may be used, and the occurrence of underground water supplies.

The type, structure, composition, and hardness of rocks present may be relatively insignificant for some uses but vitally important for other.

Each stone deposit is unique and presents its own geologic problems. However, most geologic investigations of an area must include the following determinations prior to exploitation: (1) size, shape, and character of the deposit, (2) thickness and nature of overburden and the topographic conditions, (3) degree of uniformity in composition both vertically and laterally and type and nature of impurities (4) uniformity of physical properties, and (5) ground water table levels.

Mining and Processing

Though surface quarries can be operated at lower costs than underground mines, conditions do not always permit their development. The chief factors causing the development of underground operations are heavy overburden of earth and inferior rock; steeply inclined formation that results in an increasing depth of overburden in the direction of the dip; and exhaustion of surface deposits. Underground mining has the following advantages over most quarry operations: Avoidance of stripping; production of a cleaner stone free from overburden contamination; and protection of personnel from inclement wheather, permitting steadier year-round operations. Its disadvantages are it is usually more costly to mine and transport; there is a greater investment in equipment; and 20 to 25 percent of the rock must be left in supporting pillars.

A variety of mining and quarrying methods utilizing all types of equipment, both stationary and portable, are employed. In obtaining broken stone from both quarries and mines, the following series of operations is necessary: (1) stripping or driving underground entries; (2) drilling holes for explosives; (3) blasting the stone loose; (4) loading it into trucks and cars; and (5) conveying it to the crushers.

Each of these stages of production has many fundamental problems that must be solved in order to maintain crushed stone in the same low price range as competitive materials.

More detailed data on quarrying and mining stone can be found in "The Stone Industries" (*16*), the Crushed Stone chapter of the volume "Industrial Minerals and Rocks" (*24*), and in Bureau of Mines Information Circular 8184 (*17*).

The extent of processing required is governed by the use to which the crushed product is applied. For riprap, stone must be specially selected but comparatively little preparation is required. Most applications of stone require that it be prepared according to rigid specifications: Concrete and road aggregates must be crushed, cleaned, and graded to specified sizes; pulverized stone is frequently used in processes requiring a fineness of 65 to 100 percent passing a 200-mesh screen.

Shell is considered a part of the stone industry, but the mining methods are more nearly related to those used in the sand and gravel industry.

The preparation of crushed stone products involves a series of crushing, screening, and classification operations. The primary crushers normally employed are of the jaw or gyratory type; however, if the stone is relatively nonabrasive, impact crushers are sometimes used. It is common practice to install the primary crusher in the quarry or mine, conveying the crushed stone by belt to a surge pile outside the production area, which provides a source of supply in all types of weather and during quarry and mine shutdowns. Secondary crushing usually is achieved in cone crushers and high-speed gyratories. Hammer mills are also used on the less abrasive stone.

Many industrial applications of stone require an even finer gradation. Fine crushing

of the stone usually is done with gyratories, double-roll crushers, and rod mills. The swing hammer mill is also considered a fine grinder and is used to produce such products as agricultural limestone and poultry grits of relatively coarse size. The selection of grinding equipment is based upon the characteristics of the stone and the degree of fineness specified. Pulverized stone is generally produced in grinding mills—rod mill, ball mill, tube mill, or roller mill. Closed circuit grinding, along with air classification, is employed when extreme fineness is required. Owing to the low prices of stone products, the dry grinding process is preferred to the wet process and occasionally the stone is dried (in a rotary dryer) to assure better grinding operation.

Grinding or classification operations on the smaller sized stone normally employ screens of various types. Larger stone fragments are sized with bar grizzlies, steel mesh, and perforated steelplate. Air separation is employed in classifying fine particle-sized material.

Crushed and ground materials are usually transported through the plant by belt conveyor and bucket elevators; although drag, screw, and pneumatic conveyors are used occasionally.

In former years, crushed stone was seldom washed, but washing is becoming more generally practiced. A common method of washing, if the stone is merely coated with dust, is to use water jets upon the stone during its passage over the screens. Scrubbers, used to remove adhering coatings, consist of a cylindrical or conical shell fitted with lifting plates to agitate the material and carry it forward. Chains sometimes are suspended inside the shell to increase attrition.

Highly efficient portable plants, mounted on pneumatic-tired wheels, are becoming more popular in certain regions. Such plants are used in locations where freight rates on stone produced at permanently established plants make its cost prohibitive. One advantage of the portable or semiportable plant, in addition to saving transportation cost on stone, is that it can be moved from point to point on the deposit with the result that selective quarrying may be employed. Use of smaller crushers, however, requires greater fragmentation in blasting and is reflected by increased drilling and blasting costs. There is also frequently a waste in stone sizes that cannot be used on a specific project.

Uses

About 71 percent of the crushed stone produced is limestone which has a much greater variety of uses than other rocks. Large quantities are used for cement, lime, furnace flux, agriculture, and a great variety of chemical and industrial applications, such as alkali, glass, paper, and sugar manufacture. Table 4 gives quantities of stone sold by end use, in the United States, during the 1954–63 period. About 11 percent of the total consists of basalt (trap rock), about 7 percent granite, and the remainder sandstone, marble, shell, quartzite, marl, slate, and miscellaneous rocks. Concrete aggregate and roadstone are the major uses, consuming 64 percent of the total. About 14 percent was utilized as a cement raw material. Riprap, fluxing stone, and agriculture used about 4 percent each. Table 5 shows types of stone sold in 1963 by end use.

Byproducts and Coproducts

During the crushing process most crushed stone quarries produce an excess of fines that are sold as byproducts. The development of stone sand for use as fine aggregate has solved this disposal problem at many plants. Some quarries now produce fine materials exclusively. Often the weathered overlying rock that occurs at most quarry operations can be sold as "crusher run" material for use as road base. A number of dimension stone quarries and mines producing metallic ores process waste stone piles or tailings for sale as aggregates or other purposes.

The crushed stone industry is becoming more interested in diversification including concrete products, ready mixed concrete, and asphalt plants in order to sell service and to dispose of surpluses profitably.

TABLE 4.—*Crushed and broken stone sold or used by producers in the United States, by major uses*

[Thousand short tons]

Year	Concrete and roadstone	Cement	Flux	Agriculture	Calcined lime and dolomite	Riprap	Railroad ballast	Refractory	Other uses	Total
1954–58 (average)	273,720	81,665	35,390	19,523	16,581	12,314	14,782	1,265	35,499	490,737
1959	357,098	91,010	28,633	20,819	20,517	16,904	11,314	955	34,471	581,721
1960	387,084	85,551	31,878	22,804	19,724	23,963	11,158	749	31,716	614,527
1961	387,107	85,314	27,623	22,444	19,544	27,085	9,617	697	30,140	609,623
1962	414,970	89,651	26,512	23,269	20,797	36,415	11,042	711	30,858	654,225
1963	439,325	93,299	27,630	26,216	22,619	30,200	11,727	1,180	33,554	685,750

TABLE 5.—*Crushed and broken stone sold or used by producers in the United States 1963, by kinds and principal uses*

[Thousand short tons and thousand dollars]

Kind of stone	Quantity	Value	Quantity	Value	Quantity	Value	Quantity	Value	Quantity	Value
	Concrete and road-stone		Cement		Flux		Agriculture		Lime and calcined dolomite	
Granite	41,756	$60,881					(1)	(1)		
Basalt	61,661	93,717								
Marble			(1)	(1)			(1)	(1)	(1)	(1)
Limestone	292,976	380,893	86,842	$92,646	27,185	$39,322	25,956	$44,195	21,450	$36,024
Shell	11,821	17,277	5,278	5,847			(1)	(1)	1,169	1,663
Marl			904	811			260	178		
Sandstone, quartzite, and crushed quartz	17,239	27,595	(1)	(1)	442	1,704				
Slate										
Miscellaneous	13,872	18,423			(1)	(1)	(1)	(1)		
Total	439,325	598,786	[2] 93,024	[2] 99,304	[3] 27,627	[3] 41,026	[3] 26,216	[3] 44,373	[3] 22,619	[3] 37,687
	Riprap		Railroad ballast		Refractory		Other		Total	
Granite	1,843	$3,469	1,987	$2,376			2,454	$4,111	48,040	$70,837
Basalt	8,094	9,931	1,784	2,735			1,326	4,535	72,865	110,918
Marble							1,752	13,565	1,752	13,565
Limestone	10,690	13,229	4,923	6,410	769	$1,297	17,557	47,910	488,348	661,926
Shell							751	4,633	19,019	29,420
Marl									1,164	989
Sandstone, quartzite, and crushed quartz	6,020	5,140	991	1,115	411	5,040	3,463	5,978	28,566	46,572
Slate							749	3,310	749	3,310
Miscellaneous	3,553	4,213	2,042	1,418			5,780	10,199	25,247	34,253
Total	30,200	35,982	11,727	14,054	1,180	6,337	33,832	94,241	685,750	971,790

[1] Included with "Other."
[2] 275,000 tons valued at $384,000 included with "Other."
[3] Minor quantities included with "Other."

Alternate Materials

Sand and gravel and iron-blast-furnace slag are interchangeable with stone under many construction specifications; therefore, competition is very keen in areas where these occur together, and profits are usually held to narrow margins. Lightweight aggregates are moving into the field more and more, particularly where a saving in steel is desired. When high strengths are not required, a lightweight material comparable in price with stone can usually be furnished. Slag is competitive with stone in making cement and mineral wool.

Reserves

U.S. reserves are large but stone deposits of the character or quality required to meet specifications for a particular use are limited in some areas. Crushed stone is a high-bulk, low unit value commodity and its economic utility, therefore, is restricted by its ability to compete on a delivered price basis with alternate materials or sources. Availability and cost of transportation often determine whether a particular deposit is or is not a commercial reserve. For example, a new road, in addition to being a market for crushed stone aggregate, may provide a new transportation route to contiguous market areas where stone from a particular deposit could not previously compete because it was inaccessible. Local shortages in rapidly urbanizing areas exist owing to zoning restrictions imposed as build-up areas encroach upon existing quarries and because buildings occupy ground that otherwise might have been worked for stone in the future. This rapid expansion of metropolitan areas, however, is not all negative in its effect. As suburbs spread outward some quarries are forced out of business either because they are judged a nuisance or as land values spiral; but in the annular belt beyond the suburbs stone deposits, previously not economic, become profitable to operate as burgeoning markets are created by the nearby construction. The older inner core of the city presumably now built up and with less current need for aggregate must reach further out for stone supplies it is true, but with high land values in city centers, a rising cost for aggregate is not a limiting factor in determining project feasibility.

Metallurgical or chemical-grade stone is a special case with definitely restricted distribution of deposits. Discovery of new sources is becoming increasingly difficult and expensive. While no shortages exist at this time, judicious use of available stone should be practiced to ensure future supplies.

Sources of Statistical Information

Statistical data on stone are acquired by the Bureau of Mines from the individual producer and from government agencies. The smaller elements of the industry are sporadic in operation and transient in nature. Production and consumption of crushed stone are virtually synonymous, as stocks are moderate and more or less constant. Information is collected on various types of stone and the size and type of plant and productivity rates. Results of these compilations are published annually as a chapter in the Bureau of Mines Minerals Yearbook. A distinction is made between commercial and noncommercial production. Import and export data are furnished by the U.S. Department of Commerce.

Production, Consumption, and Trade

Crushed stone is a low-priced commodity and consequently most of it is shipped as it is produced, without extensive stockpiling. Some of it is stockpiled, however, to meet peak demands and to provide for the variation in demands for different sizes. There is not much variation in the total stocks carried, although the stockpiles are apt to be larger at the beginning of a construction season. There is very little difference in tonnage of stone produced and consumed during the year.

The accompany tables 4, 5, and 6 give the output of crushed and broken stone (including shell) in the United States, classified as to uses and types.

Imports of crushed stone are small. They consist chiefly of chalk and whiting from Europe and quartzite from Canada. Exports are small and consist mostly of limestone to Canada.

Tariff rates for crushed stone differ according to type and use of stone. In general, for important rock types, granite and quartzite are admitted free, limestone is subject to a duty of 20 cents per short ton, marble is 10 percent ad valorem, slate is 10.5 percent ad valorem, and stone not specially provided for is free. Rates for some types are somewhat higher if supplied by Communist nations.

Government Programs and Legislation

Federal safety standards must be adhered to by crushed stone quarry operators. Zoning legislation by State and local governments restricts the mining and processing of stone near cities.

Prices, Costs, and Productivity

Unit values are relatively low and have not advanced as much as prices of commodities in general. This is a result of the constant pressure applied by competition and the benefits from increased efficiency of production. The price of crushed stone at the plant is only slightly higher than 25 years ago and substantially below the average increase in costs of other construction materials. The average value per short ton reported in 1963 was $1.42. Depending upon type of stone, end use, and location, actual market prices varied appreciably. Prices for crushed stone used in concrete are published for individual market areas each month in Engineering News-Record.

Comparative costs of operations depend upon many variables including efficiency of management, type of deposit and character of the rock, mining method, condition of equipment, complexity of processing plant, distance from market, and volume of material sold. It is estimated that about 40,000 persons were employed by the crushed stone industry in 1963, indicating productivity in excess of 17,000 short tons per man year.

Strategic Considerations

Since crushed stone is vital to the construction, chemical, and metallurgical industries, crushed stone must be considered in mobilization planning.

TABLE 6.—*Average values per short ton of crushed and broken stone sold or used by producers in the United States, by uses*

Year	Concrete and roadstone	Cement	Flux	Agriculture	Lime and calcined dolomite	Riprap	Railroad ballast	Refractory	Other	Total
1954–58 (average)	$1.34	$1.05	$1.37	$1.64	$1.41	$1.27	$1.06	$6.60	$2.33	$1.37
1959	1.34	1.06	1.46	1.73	1.55	1.22	1.13	7.53	2.87	1.42
1960	1.35	1.07	1.45	1.72	1.56	1.36	1.15	8.12	1.67	1.41
1961	1.35	1.08	1.49	1.73	1.54	1.24	1.17	7.29	3.02	1.41
1962	1.37	1.11	1.45	1.70	1.68	1.15	1.21	8.01	2.70	1.43
1963	1.36	1.07	1.48	1.69	1.67	1.19	1.20	5.37	2.79	1.42

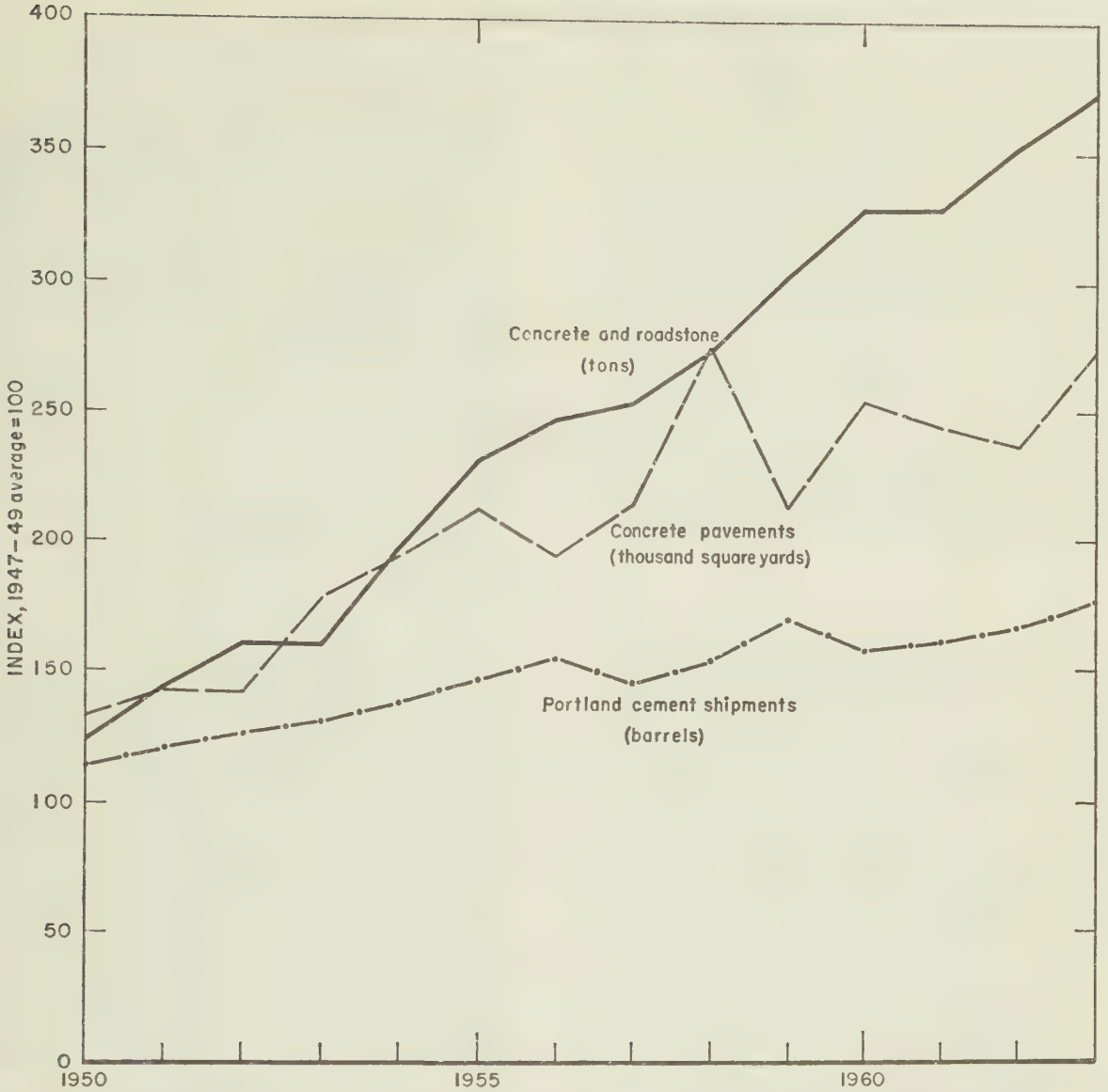

FIGURE 1.—Crushed-Stone Aggregates (Concrete and Roadstone) Sold or Used in the United States, Compared with Shipments of Portland Cement, and Concrete Pavements (Contract Awards, Thousand Square Yards).

(Data on Pavement Contract Awards from Survey of Current Business, U.S. Department of Commerce.)

The problems, however, do not evolve from raw material self-sufficiency. They are primarily in the fields of production capacity in localized areas or availability of transport and fuel to move essential stone to where it is needed.

Taxes

Crushed or broken stone is allowed a 5 percent depletion rate. Exceptions are chemical and metallurgical stone, which are granted the 15 percent rate.

Transportation

Crushed stone has a low value per ton; therefore, transportation is a major factor in the economics of the industry and sometimes makes up more than two-thirds of the delivered price. There has been a marked trend toward increased truck transportation for many years. It is conceivable that the railroads might win back some of their lost haulage as plants are removed farther from metropolitan centers. New railroad innovations such as unit trains

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and articulated cars have lowered transportation charges in some instances and have served to help the railroads compete with highway haulage. On the other hand, the tendency toward utilization of portable plants has shortened the distance of transport. Imposed restrictions on the wheel loads permitted over highways prevent highway use of large capacity trucks used in some quarries. Water transport is of great importance in some areas, notably from the quarries of northern Michigan and in the New York City metropolitan area.

Research

Because of the basic nature and broad economic impact of the crushed stone industry, widespread research is conducted on all facets of the commodity from raw materials and mining through utilization. The industry, industry associations, equipment manufacturers, universities, and Federal and State agencies have prominent roles in various components of the overall research effort.

Among groups that deserve mention are the American Society for Testing and Materials, the American Association of State Highway Officials, The National Crushed Stone Association, The National Limestone Institute, The National Ready-Mixed Concrete Association, the National Bureau of Standards, the U.S. Army Corps of Engineers, the Bureau of Public Roads, the Bureau of Reclamation, and the Bureau of Mines.

The results of the intensive research are too numerous to mention here. But keener knowledge of the basic properties of materials, improved testing methods, more vigorous and correct specifications for various uses, better equipment and plant design, all have been among the benefits accrued from the dedicated efforts of many scientists and engineers.

OUTLOOK

Based upon anticipated or planned public and private construction and continuation of various highway building programs, the quantity of crushed stone produced may be expected to increase yearly for some time to come. Increased effort will be made by Federal road planners to speed up work in areas where construction of the Interstate Highway System appears to be lagging. Further expansion of the roadbuilding program appears to be imminent with an accompanying demand for more road aggregate. Changes in roadbuilding technology caused by heavier and faster traffic also will increase demand for roadstone; currently more stone is used for wide and heavy shoulders than for the pavement itself. The proportion of concrete work poured on the job will decrease as use of precast concrete units such as wall panels, complete with window and door openings, are produced by factory methods and brought to the building site to speed up construction and lower labor costs. Greater use will be made of lightweight concrete products, exposed aggregate panels, prestressed concrete, and aerated concrete.

Expanding use in the iron and steel industry of self-fluxing iron pellets or sinters, in which limestone is added during processing, may reduce quantity of limestone used as direct flux in the blast furnace. Expansion of Linz-Donawitz and basic-oxygen processes for steelmaking also will change previously established patterns for production and use of limestone.

Present trends in methods for producing crushed stone, which tend to improve efficiency and reduce costs, include greatly increased load capacity for off-the-road trucks; improved blasting techniques designed to avoid secondary blasting and to decrease claims for blasting damage; increased capacity, complexity, and mobility of portable plants; expanding use of tractor-drawn rippers to break ledge rock for loading; greater use of impact crushers to produce cubic road aggregate and to cut down waste owing to production of unacceptable flats and splinters; improvements in methods which are designed to reduce stockpile segregation; greater use of automatic and pushbutton controls and closed-circuit television systems to control all phases of processing; and increased concern by producers about methods for control of dust, water pollution, and noise in quarry operations.

Closer supervision of many quarry operations by various government agencies is foreseen, particularly as regards blasting, speed and weight of trucks operating on streets and public highways, and in noise, dust, and pollution abatement.

No new uses for crushed and broken stone are in prospect. New quarries to produce aggregate for local buildings are frequently opened and abandoned as programs are completed. Larger, well-established quarries will expand and modernize equipment as demand increases. Shipping radii of quarries will increase through use of innovations such as unit-trains and articulated railroad cars.

Estimated production of crushed and broken stone in 1980 is 1.5 billion tons.

PROBLEMS

There is pressing need for simplification and standardization of specifications for crushed stone aggregate. In the 50 States there are 215 dissimilar gradations specified for coarse aggregate to be used in portland cement concrete, and 58 specifications for fine aggregates. No uniform method is in actual use by the various States for designating aggregate gradation sizes. Suppliers would find it simplier and less costly if specifications for Federal, State, county, and municipal purchases, at least in similar areas, used identical specifications for the same type of construction.

There is little general understanding of the relationship between physical and chemical makeup of crushed stone aggregate and performance of concrete in which it is used.

Continuing problems are those related to (1) improving efficiency of drilling and blasting operations; (2) most efficient methods for plant layout; (3) location and rating of economically workable deposits; (4) removal of overburden; (5) control of noise, dust, and other annoyances to avoid restrictive zoning legislation; and (6) increasing insistence upon land rehabilitation.

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STRONTIUM

By Paul M. Ambrose [1]

THE PRINCIPAL strontium minerals are celestite ($SrSO_4$) and strontianite ($SrCO_3$). These minerals occur in several States, and the principal deposits are in Texas, California, Arizona, and Washington. Domestic production is small and irregular. Reserves are large compared with current consumption. The market is small, and in most areas the cost of preparing the mineral for market and transporting it to the principal consumers discourages competition with strontium minerals from the United Kingdom and Mexico. Imports in 1963 totaled 16,232 short tons valued at $372,024.

Strontium minerals are usually mined by open-pit methods and beneficiated by hand picking or by simple gravity concentration. Most strontium is consumed as compounds. It is used principally in flares, fireworks, and tracer bullets because of the brilliant red it imparts when burned. Other uses are in fusees, ceramics, medicine, beet sugar, electronic tubes, purifying caustic soda, and refining zinc (*10*).[2]

Strontium mineral supplies probably will continue to come from foreign sources. Moderate increases in consumption are expected. Development of new uses and the utilization of domestic sources are problems of the industry.

BACKGROUND

Commercial production of strontium minerals and compounds began in Germany about 150 years ago. Strontianite from Westphalia was converted principally to the nitrate for use in pyrotechnics. Demand for strontium increased greatly with the introduction of the process for using the hydroxide in recovering sugar from beet-sugar molasses. Commercial production of celestite began in England in 1875, and until World War I most of it was shipped to Germany for conversion. In Germany, output of strontianite declined but production of celestite increased.

During World War I when German supplies were not available, facilities were established in the United States for processing strontium minerals from England. Domestic production increased substantially during World War I, but production of strontium minerals has been sporadic and small since then, except for a relatively large tonnage of low-grade material mined for well-drilling mud when there was a royalty on barite for this purpose. Most supplies of strontium minerals have come from England and Mexico in recent years.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Domestic production of strontium minerals in the past several years has been confined to the occasional operations of a few small firms in Washington and California. Their combined output is only a few hundred tons at most in any year, and none has been produced since 1959.

The following firms convert imported strontium minerals to various compounds: E. I. du Pont de Nemours & Co., Inc., Grasselli, N. J.; Foote Mineral Co., Exton, Pa.; and Inorganic Chemicals Division, FMC Corp., Modesto, Calif.

Strontium metal is produced in the United States by King Laboratories, Inc., Syracuse, N.Y.; however, only small quantities are made.

[1] Commodity specialist.
[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Two strontium minerals are important commercially. The more important of these, by reason of its greater abundance and more widespread occurrence, is celestite ($SrSO_4$), which contains 56.4 percent strontium oxide (SrO). Strontianite ($SrCO_3$), containing 70.1 percent SrO, has a higher strontium content but is less abundant and often occurs with celestite. Strontianite can be reacted directly with acids, but it often contains calcium and thus is frequently not suitable for producing high-purity strontium chemicals.

Although specifications are variable, consumers of celestite for conversion to strontium chemicals usually specify a minimum of 92 percent $SrSO_4$, a maximum of about 4 percent calcium sulfate ($CaSO_4$), and a maximum of about 4 percent barium sulfate ($BaSO_4$). Imported material is usually about 94 to 97 percent $SrSO_4$. The specifications for celestite for use in purifying zinc or in drilling mud are not so stringent as for chemical use.

The purchase specification for celestite for the national stockpile (P–10–R2, Sept. 28, 1960) provided that each lot of celestite purchased under the program should not contain more than 2 percent free moisture, not less than 95 percent strontium sulfate ($SrSO_4$), not more than 1.5 percent calcium, as sulfate ($CaSO_4$), and not more than 2 percent barium, as sulfate ($BaSO_4$). This specification states, "All celestite shall be in the physical form that is normally supplied to, and suitable for processing by, industry." The former specification (P–10–R1, Dec. 10, 1956) required that all celestite be either lump or pebble ore, all of it should be in bulk, and not more than 2 percent by weight should pass a U.S. Standard Sieve No. 4.

TECHNOLOGY

Strontium in small quantities or traces is common in igneous rocks and less abundant in sedimentary rocks. Most commercial or potentially commercial deposits of strontium minerals (celestite and/or strontianite) occur as beds, veins, veinlets, nodules, or irregular masses in or near sediments or sedimentary rocks. In Texas, celestite is found in three areas. The first and probably most important area is in Nolan, Fisher, Coke, and Taylor Counties; the second is in Somervell, Erath, Comanche, Brown, Mills, Lampasas, Burnet, Williamson, and Travis Counties; and the third is in Real and Uvalde Counties (*5*). In these areas celestite occurs as beds, veinlets, nodules, or masses in sands, clays, shales, or dolomitic limestones.

Celestite and strontianite occur together in Skagit and Whatcom Counties, Wash. (*8*). Certain limestones in Ottawa County, Ohio, contain veins and masses of celestite. Deposits of celestite occur in Maricopa County, Ariz., one in the Vulture Mountains and another a few miles south of Gila Bend. Several celestite deposits occur in arid south-central California. Celestite occurs a few miles south of Ocotillo, San Diego County; along the edge of Bristol Dry Lake in San Bernardino County; near the southern end of Death Valley; and in the Cady Mountains north of Ludlow in San Bernardino County (*2*). Strontianite occurs in the Mud Hills near Barstow.

Strontium minerals are recovered by simple methods on a small scale. The very small tonnage occasionally mined in the West is concentrated by selective mining and hand picking. The material formerly mined in Texas was broken from the deposit by horse-drawn plows, sorted, and handloaded. During World War II, a domestic firm processed this ore by grinding and tabling. The concentrate obtained was relatively low grade, and production was discontinued when higher grade foreign material became available. The Bureau of Mines conducted research on a flotation process for recovering celestite from Texas ores.

In England and Mexico, the ore is mined by simple methods in shallow open pits or from veins exposed in the stopes of metal mines. Usually the celestite is handpicked. Gravity concentration has been employed in the English operations in recent years.

Most of the strontium minerals consumed are converted to various chemical compounds. A common procedure is to digest finely powdered celestite in a hot soda ash solution to produce the less soluble strontium carbonate, which is treated with the appropriate acid to make the desired salt. Another method is to burn finely powdered coal with celestite to produce a soluble strontium sulfide, which is leached from the clinker with water and filtered. The solution may be treated with carbon dioxide to produce the carbonate; or with nitric acid to produce the nitrate. Strontium metal is produced by thermal reduction of strontium oxide with metallic aluminum and also by electrolysis of fused strontium chloride and ammonium chloride.

USES

There are uses for the minerals celestite and strontianite, strontium metal, and alloys of strontium, but much greater quantities are consumed as strontium compounds.

The characteristic brilliant crimson color that strontium imparts to a flame has many pyrotechnic applications. Most military uses of strontium depend on this property. The principal direct military uses are for strontium nitrate, peroxide, and oxalate in flares and tracer ammunition. In tracer ammunition, a charge containing one of the compounds mentioned previously or a combination of them, is inserted in the base of the bullet. On firing, this charge is ignited and burns brilliantly during the flight of the bullet permitting the gunner to see the accuracy of his aim.

The military use of strontium next in importance is in flares and signal devices. Flares are used for tactical and distress or rescue signaling and for illumination. They are various sizes, shapes, and types, and have red flames and usually some ejecting or propelling device.

Marine distress signal equipment consists of red parachute flares and a pistol for shooting the flares into the air. Larger distress rockets may be fired several hundred feet high, and some release showers of "stars." Similar red flares may be dropped or shot from aircraft or released by submarines.

The Federal Motor Carrier Safety Regulations require that "Carriers by Motor Vehicle" operated in interstate commerce have certain emergency equipment available at all times. These regulations require that the emergency equipment units include one of several combinations of warning devices for stopped vehicles. Among these devices are red fusees. Many States also require that fusees be carried on certain types of vehicles.

The familiar red color of many fireworks and pyrotechnic exhibitions is produced by strontium compounds.

Although Federal regulations do not specifically require it, for many years railroads have used red flares and fusees for emergency signaling as a safety practice. All railroad companies require that a number of 5- and/or 10-minute fusees be carried on each operating passenger or freight train. When a train slows down or stops, the flagman places these fusees so that following trains will be warned.

In Germany, sugar-beet molasses was formerly treated with strontium hydroxide (the Scheibler process) to recover beet sugar. The sugar was precipitated as relatively insoluble strontium saccharate, filtered, and treated with carbon dioxide. Strontium carbonate was precipitated and recovered with about a 5-percent loss. The sugar solution was crystallized by evaporation. This process has been supplanted by lime and barium hydroxide processes.

The major uses of strontium carbonate are in ceramics, principally in frits and glazes. Minor applications of strontium compounds are in depilatories, medicines, greases, metallurgy, corrosion inhibitors, plastics stabilizers, fused-salt baths, and optics.

Strontium metal and some of its alloys are getters for extracting the last traces of gases from electronic tubes. This minor use consumes only a few pounds annually.

In preparing high-purity electrolytic zinc, strontium carbonate removes lead from the cathode zinc. The minerals have been utilized in well-drilling mud, in purifying caustic soda (by adsorption of iron), and as a filler, but only a small quantity is used in the United States for any of these purposes.

ALTERNATE MATERIALS

There are no satisfactory substitutes for strontium compounds in most of their chemical and ammunition and other pyrotechnic uses. Many materials impart color to flame, but no substitute has the brilliance and visibility range of strontium compounds. The use of strontium minerals in the purification of certain grades of caustic soda has largely been supplanted by other methods.

RESERVES

Domestic deposits have not been explored thoroughly, but reserves in the investigated deposits have been estimated by the U.S. Geological Survey at 3.5 million tons of material containing 85 percent or higher $SrSO_4$. When considering reserves, it is important to know whether the material can be mechanically beneficiated to chemical grade. Some celestite contains calcium and barium so intimately locked within the crystal lattice that these elements cannot be removed except in a chemical process.

Little is known of reserves in foreign countries. Deposits are worldwide, and reserves in several deposits are substantial in terms of current and anticipated requirements.

SOURCES OF STATISTICAL INFORMATION

Figures on domestic and world strontium mineral production and strontium mineral imports by country of origin are published annually in the "Strontium" chapter of the Bureau's Minerals Yearbook.

PRODUCTION, CONSUMPTION, AND TRADE

Domestic production is small and sporadic. The quantity of strontium minerals sold or used ranged from 50 short tons in 1953 to over 4,000 short tons in 1956. There has not been any domestic production for 5 years.

The United States depends almost solely on imported celestite to satisfy the demand of the domestic strontium chemical industry. Imports are given in table 1.

Celestite and strontianite have always been on the list of materials that may be imported into the United States free of duty. The duty rate for strontium carbonate (precipitated), strontium nitrate, and strontium oxide is 12.5 percent ad valorem. Duty rate for other strontium compounds is 10.5 percent. The rate for strontium metal is 10 percent ad valorem, and for strontium alloys, 15 percent ad valorem.

TABLE 1.—*Strontium minerals* [1] *imported for consumption in the United States*

Country of origin	1954–58 (average)		1959		1960		1961		1962		1963	
	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value
Italy	2	$593	11	$2,700	11	$2,700	11	$2,700	27	$6,750	11	$2,700
Mexico	2,105	28,465	2,182	39,936	2,881	56,530	2,642	48,713	4,554	98,476	6,476	104,867
United Kingdom	4,306	99,892	5,946	182,769	3,294	90,476	7,278	193,064	2,908	83,609	9,745	264,457
Total	6,413	128,950	8,139	225,405	6,186	149,706	9,931	244,477	7,489	188,835	16,232	372,024

[1] Strontianite ($SrCO_3$) and celestite ($SrSO_4$).

Source: U.S. Department of Commerce.

STRATEGIC CONSIDERATIONS

If outside strontium supplies were cut off, the United States could be self-sufficient at a higher price and perhaps at the sacrifice of plant capacity, certain processing acids and reagents, and time. It is not known how much domestic material could be beneficiated to meet the specifications of the currently available foreign material nor at what price this could be done. Economics is the principal consideration when discussing self-sufficiency in strontium minerals.

Strontium compounds are considered essential in several military and civilian uses. Our almost total dependence on foreign sources of strontium minerals (even though this may be due in great part to economic reasons) has made strontium critical in an emergency. Therefore, celestite was placed on the list of materials to be acquired for the national stockpile.

The General Services Administration offered for sale, at its warehouse in Point Pleasant, W. Va., about 12,500 short tons of celestite that was part of a below-grade stockpile of 28,816 short tons. No acceptable bids were received. On June 30, 1964, Government inventories totaled 22,045 short tons, of which 13,037 tons was in Commodity Credit Corporation stocks and 9,008 tons in the supplemental stockpile. This is 214 percent of the present maximum objective.

PRICES

Trade journal prices for strontium compounds have remained constant since 1955. The 1963 prices follow: Strontium sulfate, air-floated, 90 percent, 325-mesh, bags, works, $56.70 to $66.15 per short ton; strontium carbonate, pure, drums, 5-ton lots or more, works, 35 cents per pound; drums, 1-ton lots, works, 37 cents per pound; technical-grade, drums, works, 19 cents per pound; and strontium nitrate, bags, carlots, works, $11 per 100 pounds, and bags, less than carlots, works, $12 per 100 pounds.

TAXES

Producers of celestite are allowed a depletion allowance of 23 percent on ores from domestic deposits and 15 percent on ores from foreign deposits.

TRANSPORTATION

One of the principal factors preventing the development of a domestic mining industry is the cost of transportation. The rail freight rate on celestite and/or strontianite from San Bernardino County, Calif., to Philadelphia, Pa., or Grasselli, N.J., in 1957 was about $50 per short ton. Added to the f.o.b. mine price, this makes the delivered price higher for domestic material, with a minimum of about 90 percent $SrSO_4$, than for English or Mexican celestite (95 to 97 percent strontium sulfate) which can be delivered to the same place for about $50.

RESEARCH

Industry, institutions, and Government have conducted research on various problems involv-

ing the production, processing, and utilization of strontium minerals, metals, alloys, and compounds.

During World War II, the Bureau of Mines and a domestic firm cooperated in research on the preparation of chemical-grade celestite from Texas ore. Although fair success was achieved, this domestic source was abandoned when higher grade material from foreign sources became available again after the war.

Research by industry has resulted in a recent patent on the use of ground celestite to remove deleterious materials, principally lead, from high-purity electrolytic zinc. A magnesian limestone process and an ammonia process have been devised as substitutes for celestite in the purification of caustic soda.

The Bureau has conducted a limited investigation of the physical, chemical, and thermodynamic properties of certain strontium alloys and compounds, such as strontium titanate, carbonate, sulfate, nitride, chloride, and fluoride.

OUTLOOK

For economic and quality reasons, strontium mineral supplies are expected to continue to come from foreign sources. The major sources of supply, Mexico and the United Kingdom, apparently have resources adequate for world needs for many years. Exhaustion of these resources in the distant future could force dependence on our domestic sources, which although low grade appear to be ample and technically amenable to beneficiation. Relocation of munitions plants, shifts of population and industry, and other unpredictable factors may make it economically advantageous to develop domestic deposits of strontium minerals long before foreign sources approach exhaustion.

A vast untapped strontium reserve is the earth's hydrosphere, in which strontium is the ninth most abundant element, amounting to 13 grams per ton of sea water.

Current trends in the use of strontium are difficult to discern. They involve largely new, expensive, and untried products, such as strontium titanates, and a decline for some uses, as in the purification of certain grades of caustic soda. Some unusual physical properties of strontium titanate crystals indicate that they may have special uses in optics, jewelry, and other fields. These uses, which require a very pure product, are not expected to involve large quantities of strontium.

Pyrotechnic devices will continue to be the major outlet for strontium compounds. Their use in pyrotechnics and in glass, enamels, refractories, and ceramics is likely to increase. Strontianite, or manufactured strontium carbonate, has been suggested as a flux on stainless steel welding rods. Strontium chloride as a refrigerant and an ammonia absorbent in refrigeration is another possible use. Strontium metal will continue to be used in small quantities as a getter.

Barring unforeseen substitutes or major new uses, the outlook is for short-term requirements to remain at about the current level and for long-term requirements to increase gradually and moderately.

PROBLEMS

The principal problem of the strontium industry is its dependence on a single market—the manufacture of strontium compounds for pyrotechnic uses.

Creating new uses for strontium products is a problem of interest to the mineral producers, the chemical processors, and the strontium metal producers. However, limited demand and restricted known uses offer little stimulus to the producer for costly research. Investigations culminating in short-term uses sometimes cause overexpansion of world production (new companies and mines, both domestic and foreign) which, in turn, presents the problem of accommodating idle productive capacity when the short-term use ends.

Lack of adequate information on resources and inadequate world production and consumption statistics further inhibit research programing.

The main problem of domestic strontium mineral producers, or of potential domestic strontium mineral producers, is competition from foreign sources. In addition (1) the domestic ore concentrates are presently lower in grade than the available imported material, (2) the domestic market is only a few thousand tons annually, and (3) the cost of preparation and the cost of transportation from the principal deposits in the West to the major consumers in the East is high enough to discourage competition with foreign sources. These factors provide little incentive for developing domestic deposits.

Information is needed on the properties of strontium metal and its alloying characteristics to enable evaluation of its potential in metallurgy.

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SULFUR AND PYRITES

By Paul M. Ambrose[1]

SULFUR has many uses including cellulose products, chemicals, dyes, fertilizers, iron and steel, pharmaceuticals, rubber, and water treatment, but there is a dearth of information regarding the total number of uses. New applications are being found, and any precise statement would be incorrect when made and out of date before publication. It is likely that there are thousands of uses for sulfur and sulfur containing compounds.

Per capita sulfur consumption in any country has long been a reliable index of total chemical production. Sulfur use is closely related to the industrial activity of any nation. The average annual per capita consumption in 1963 in the United States was 81 pounds, in other developed countries 56 pounds, in the entire world 21 pounds, and in less industrialized countries 3 pounds.

The United States obtains sulfur from native sulfur deposits, pyrites, other metallic sulfide ores, sour natural gas, petroleum, and coal. Imports of sulfur from Mexico and Canada are important sources of supply. Exports slightly exceed imports.

Native sulfur deposits mined by the Frasch hot-water process are the major source of supply. Sulfur from sour natural or refinery gases is growing in importance and is competitive with Frasch sulfur. Definite quantitative information on reserves of Frasch sulfur is not available. Growing recovered sulfur production and imports should gain, but ultimately other sources of supply will need to be developed.

Annual production of sulfur in all forms in the United States was 6.6 million long tons in 1963, valued at $125 million. Production averaged 6.8 million tons per year for the period 1954–63. In 1963, 74 percent was produced by 4 firms mining 10 dome deposits in Texas and Louisiana, and 62 firms at 86 plants and mines reported the remainder of the production in the United States.

The rapid growth of the Mexican Frasch, French recovered, and Canadian recovered sulfur industries since they began in 1954, 1957, and 1951, respectively, resulted in overproduction which was finally brought near equilibrium in 1963. Competition for markets was keen and prices weakened in 1961 and 1962.

The shipment, storage, and use of liquid sulfur began in 1959; the practice developed rapidly and in 1963, 85 percent of shipments were in liquid form. Oversea shipments were introduced in 1964.

The base of supply has broadened appreciably with an increase in number and size of producers. The number of brimstone producers is increasing constantly.

The industry has many problems, including competition from Canada, Mexico, and France; unequal competition between nations in restrictions; and trade barriers to exports but none to imports. Other problems involve reserves, production processes, and need of additional market research information.

BACKGROUND

Sulfur was used by the Egyptians to bleach linen textiles in 2000 B.C., but it did not become commercially important until the development of the Leblanc soda ash process in France in 1791. The sulfuric acid industry, which has consumed most of the sulfur produced, was started by John Harrison of Philadelphia in 1793. Sicily held a virtual monopoly on the sulfur trade before the beginning of the 20th century. Sulfur was mined from pits up to 500 feet deep by miners climbing circuitous steps while carrying the sulfur on their shoulders. Pay was 7 or 8 cents per day. Sulfur was recovered by burning part of the sulfur

[1] Commodity specialist.

to melt the remainder. In 1833, a depression in Sicily and the resulting hardship to producers caused the King of Sicily to grant a monopoly of the Sicilian sulfur trade to a commercial firm which raised the price of sulfur from $25 to $75 per ton. Consumers switched to pyrite as a source of sulfur, and by 1886 use of sulfur was principally for the manufacture of gunpowder, bleaching agents, and medical compounds. Dr. Herman Frasch, successfully mined sulfur at Sulphur Mine, La., by a unique hot-water melting process after several attempts to use conventional mining processes had failed. The Union Sulphur Co., which Dr. Frasch helped organize, produced the world's first Frasch process sulfur in 1895. After its deposits at Calcasieu Parish, La. were exhausted in December 1924, Union Sulphur began producing at Boling, Wharton County, Tex., in 1928.

In November 1912 Freeport Sulphur Co. began operations at Freeport, near Bryanmound, Brazoria County, Tex. On March 19, 1919, Texas Gulf Sulphur Co. began producing at Gulf, near Matagorda, Tex., using the Frasch method. The company's Boling dome, the largest producer of sulfur and also the largest salt dome ever found to that time, was started on March 20, 1929, in southeast Wharton County, Tex. In 1928 the Duval Texas Sulphur Co. began producing at Benavides, Duval County, Tex.

The United States became the world leader in sulfur production in 1913. It has maintained this lead since. In 1948–49 world demand for U.S. native sulfur exceeded mine capacity and stocks declined. A sulfur shortage in 1950, about the beginning of the Korean war, shocked the industrial world. Consumption of elemental sulfur had been greater than production since 1942. Sales restrictions and increased use of pyrite began.

In 1952 U.S. Export-Import Bank loans to the Mexican companies, the Mexican Gulf Sulphur Corp., no longer in operation, and the Pan American Sulphur Co., started Mexico to prominence as a sulfur producer. Production from both companies began in 1954, and Gulf Sulphur Co. began producing in 1956. World Frasch production grew to 6.3 million tons in 1963. Treatment of sour natural gases in Alberta, Canada, produces sulfur as a byproduct. Starting in 1951, this industry grew to 1.9 million long tons per year in 1963; future growth will be determined by natural gas sales.

Production of recovered sulfur from sour natural gas, from the Lacq field in France, began on April 21, 1957, and grew in planned stages to 1.4 million tons in 1963.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

The United States is both the largest producer and consumer of sulfur in the world. Most of the production comes from 10 Frasch process mines operated by 4 firms in Louisiana and Texas. A small quantity of sulfur ore was also mined in California and Nevada in 1963. The second most important source is recovered sulfur from the purification of sour natural or refinery gas. This industry is growing. Plants are located in 19 States. Most sulfur is consumed first in the production of sulfuric acid which is then used in a great variety of ways. Pyrite and other metal sulfides are smelted and the sulfur dioxide produced is converted to SO_3 then to acid. Smelters producing acid are located in 19 States. The use of both elemental sulfur and sulfur from metal sulfides is growing. The quantity of elemental sulfur consumed in the United States is about 13 times that of sulfur from pyrites at the present time. The more rapid growth of the elemental sulfur industry than the pyrite industry has, in the past, been due to increased need for strong acid and the availability of low-price elemental sulfur. Sales of liquid sulfur began in 1959 and have grown to 85 percent of the total in 1963. Costs usually include transportation of the liquid sulfur by the sulfur companies from the mines to liquid sulfur terminals. Such transportation is by barge on inland waterways, by rail, by truck, and by oceangoing liquid sulfur carriers. The sulfur companies own or lease ships for this purpose. Shipments outside North America are made by the Sulphur Export Corp. (Sulexco). Freeport Sulphur Co. owns 37 percent of Sulexco; Texas Gulf Sulphur Co., 37 percent; Jefferson Lake Sulphur Co. (a subsidiary of Occidental Petroleum Corp.), 18 percent; and Duval Corp., 8 percent. Shipments of liquid sulfur overseas started in 1964 after two liquid sulfur carriers, the *Naess Texas* and the *Naess Louisiana*, were completed. Imports of sulfur from Canada and Mexico increased rapidly in the last decade.

Sulfur is recovered from the sweetening of sour natural gas at 15 plants in Alberta, and 1 plant each in British Columbia and Saskatchewan. A capacity of 1.9 million tons was not fully in use in 1963, but additional capacity was to be created with time as natural gas markets expand. Lowered freight rates from Canadian sulfur sources to the upper Midwest have been an important factor in expanding Canadian sulfur sales.

Mexican Frasch production has grown stead-

ily and capacity is presently being expanded from 1.9 to 2.5 million tons.

French recovered sulfur from sour natural gas is produced by Société Nationale des Pétroles d'Aquitaine from the Lacq area of France. Planned production capacity of 1.4 million tons has been reached, and expansion has been restricted for reasons of conservation. France has started to deliver liquid sulfur in Europe to meet U.S. Frasch competition there. Liquid sulfur terminals are located at Rotterdam, Holland, Immingham, England, and Rouen, France.

DEFINITIONS OF TERMS, GRADES, AND SPECIFICATIONS

Native sulfur is sulfur that occurs in elemental form in nature. *Frasch sulfur* is native sulfur mined by the Frasch hot-water process.

Recovered sulfur is elemental sulfur produced from hydrogen sulfide obtained from sour natural gas, petroleum refinery gas, water gas, and other fuel gases.

Pyrites is a not-too-well-defined term which includes a number of metal sulfides usually pyrite (FeS_2), marcasite (FeS_2), and chalcopyrite ($Cu_2Fe_2S_4$).

Crude sulfur or *brimstone* is elemental sulfur that is 99.0 to 99.9 percent pure and is free from arsenic, selenium, and tellurium. Run-of-mine Frasch sulfur contains about 50 percent fines, with lumps to 8 inches in size.

Amorphous sulfur is the insoluble residue used in the vulcanization of rubber and is produced by extracting flowers of sulfur with carbon disulfide.

Colloidal sulfur is a suspension of fine sulfur particles in water.

Flowers of sulfur is crude sulfur refined by sublimation.

Precipitated sulfur is sulfur precipitated from calcium polysulfide solutions by hydrochloric acid and washed to remove all calcium chloride.

Wettable sulfur is sulfur treated so that it is easily dispersed in water.

Paste is a slurry of sulfur and water, usually containing 30 to 50 percent of finely divided elemental sulfur.

Dark sulfur is crude sulfur containing up to 1 percent oil or carbonaceous material and is dark in color. *Bright sulfur* is crude sulfur free of discoloring impurities and is bright yellow in color.

TECHNOLOGY

Geology

Sulfur is widely distributed in nature in the free and combined state. The lithosphere and hydrosphere contain approximately 0.06 and 0.09 percent sulfur, respectively, and the average content of the lithosphere, hydrosphere, and atmosphere is 0.06 percent. Meteorites from outer space and practically all animal and plant life on earth also contain sulfur. Sulfur combines directly with most other elements, both metals and nonmetals, except nitrogen and the inert gases. Concentrations of surfur or sulfur compounds of commercial importance are much more restricted in distribution. Such economic deposits mined for their mineral value include native sulfur, sulfide, or sulfate minerals. By far the most important deposits of native sulfur occur as crystals of sulfur disseminated through a limestone or gypsum host rock. The Frasch process mines along the coast of the Gulf of Mexico and the sedimentary deposits of Poland, U.S.S.R., and Sicily are of this type. The way in which these deposits were formed has not been established definitely, but the sulfur may have been produced by the chemical reduction of gypsum, possibly through biochemical reactions.

Other native sulfur deposits associated with volcanic activity are smaller in size but are more numerous and widespread. In these deposits sulfur was released when hydrogen sulfide gas was oxidized or sulfur dioxide and hydrogen sulfide gases reacted to produce sulfur and water. Metal sulfide deposits mined primarily for the metal content also are important sources of sulfur dioxide to produce sulfuric acid and in some cases elemental sulfur. The largest potential sulfur resources occur as gypsum, calcium sulfate. Gypsum is not used in the United States as a source of sulfur but has been used in England, India, and formerly in continental Europe and probably will become important in the future. An enormous deposit of sulfur occurs with the Athabasca oil sand in Alberta, Canada. The oil sands are about to be mined and some sulfur should be produced by 1970.

Deposits Associated With Salt Domes

Salt domes occur in the United States, Mexico, West Germany, Rumania, U.S.S.R., Iran, and other countries. In the United States salt domes extend from Alabama (McIntosh salt dome) on the east, westward through Mississippi, Louisiana, and Texas to near the Rio Grande River. The deposits lie within a belt which extends 75 to 300 miles inland from the gulf coast and offshore. This area has been divided into four salt basins: Gulf coast salt basin, interior domes of Texas, interior domes of Louisiana (*19*)[2] and Louisiana-Mississippi salt basin.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

A salt-dome formation consists essentially of a solid vertical column of salt, extending to great depths and forming a dome-shaped structure in the overlying sediments. The salt dome (cap and salt stock) is usually circular or elliptical in form, with a horizontal extent of a few yards to 2 miles or more. In many instances the top of the salt stock is remarkably flat and is succeeded above by a characteristic series of minerals collectively known as the cap. Sedimentary beds surrounding the core are displaced upward at sharp angles along the sides by the upward movement of the salt column. It is widely believed that the source of the salt in domes is deeply buried Cretaceous or Permian sediments, from which salt was forced upward at points of weakness. Usually the deposits are surrounded by formations that are tight enough to restrict the flow of hot water.

The cap-rock series constists chiefly of anhydrite, gypsum, and limestone. Generally, the anhydrite lies directly on the massive salt core. Limestone and gypsum occur as zones or lenses above the anhydrite.

Sulfur usually occurs as orthorhombic crystals, crystal aggregates, and disseminated particles in the lower part of porous limestone or in gypsum zones of many domes, at depths ranging from 500 to 2,500 feet. Thickness of the sulfur horizon is seldom less than 25 and sometimes reaches 300 feet. A typical deposit of commercial size may have a sulfur-bearing zone 100 feet thick containing 20 to 40 percent sulfur. Only a small proportion of the domes discovered to date have contained enough sulfur to warrant development. The porosity of the sulfur-bearing horizon is assumed to be 15 to 25 percent.

Volcanic Deposits

Deposits of native sulfur are found in most volcanic regions of the world, both active and extinct. These deposits may be formed by reaction between hydrogen sulfide and sulfur dioxide, incomplete oxidation of hydrogen sulfide, or reaction of sulfur dioxide and water. Sulfur deposits also may originate by precipitation from thermal springs, incomplete oxidation of hydrogen sulfide by oxygen, or bacterial action. The largest known deposits of this kind are in the Andes Mountains of South America. More than 100 deposits of sulfur occur at elevations to 18,000 feet in a zone 3,000 miles long parallel to the west coast of South America. These deposits are mined to a limited extent but are of interest primarily as potential resources. In Japan sulfur deposits associated with a chain of volcanoes occur on the main island. These make important contributions to the sulfur supply of Japan. Deposits from which sulfur may be recovered are also known near Lake Rotorua, New Zealand, and in Alaska, Iceland, Mexico, and elsewhere. Deposits formed by springs are found in the Western United States—Cuprite, Esmeralda County, Nev.; Rabbit Hole mines, Humboldt County, Nev.; Sulphur Bank, Lake County, Calif.; Cave Creek mine, Beaver County, Utah; and Cody and Thermopolis, Wyo., (*13*).

Sedimentary Deposits

The sulfur of sedimentary deposits comes from sulfates in rocks and from hydrogen sulfide from volcanic emanations, anaerobic bacterial decay, and bacterial reduction of sulfates in solution. These substances are transported in solution or as colloidal sulfur to sedimentation basins. The sulfur is deposited from sulfates and hydrogen sulfide in water where reducing conditions and anaerobic bacteria exist.

Two large deposits in southeast Poland are the Tarnobrzeg deposit now being mined and the Solec-Grzybow deposit as yet undeveloped. The Tarnobrzeg deposit extends from Tarnobrzeg to Piaseczno. The sulfur occurs in a Miocene sedimentary sequence with beds in order from bottom to top of clay, gypsum containing sulfur, limestone-reef, fluviatile sand, argillites, and clays. The grade of sulfur is 28 to 30 percent average with a maximum locally of 80 percent. The sulfur beds lie close to the surface. Cover is 30 feet at Piaseczno, and 77 to 87 feet at Machow. The sulfur bed is 15 feet thick at Piaseczno and 33 feet thick at Machow but is 66 feet thick in places. The second Polish deposit of interest is the Solec-Grzybow deposit in southeast Poland. This deposit is 42,000 feet east-west, and 2,100 feet north-south. Sulfur content is 20 percent at Solec where the deposit is 15 feet thick under 75 feet of overburden and 30 percent at Grzybow where the deposit is 80 feet under 550 feet of burden.

Important sedimentary deposits occur near Kuibyshev, Sukeievo, and Chekur in the U.S.S.R. These deposits are of Permian and upper Tertiary age, respectively. The deposits at Kuibyshev contain interbedded layers of pure sulfur, laminates of sulfur, and calcite or sulfur nodules in bituminous limestone between layers of gypsum.

Sicily has numerous native sulfur deposits scattered over an area 105 miles east-west by 56 miles north-south (5,880 square miles). The richer deposits were found between Gibellina on the west and Centuripe on the east, and the central one-third of the island in the north-south directions. Deposits may have existed over the entire island before erosion. The zone containing the sulfur is well defined by a Pliocene up-

lift, principally of sandstone resting on a Miocene shale. Sulfur-bearing formations lie in isolated basins up to 5 miles long and 0.5 mile wide. These formations or lenses are composed of a series of interbedded limestone and bituminous shales. Sulfur occurs as incrustations and small pockets in the limestone or as thin seams interlaminated with rock. Formations average 26 percent sulfur of brown or brownish gray color due to bituminous contamination (*2*).

Pyrites Deposits

Metal sulfides called pyrites are important sources of sulfur providing 40 percent of all sulfur produced in 1963. Leading producers were Japan, U.S.S.R., Spain, Italy, and China.

The principal minerals in the pyrites group are pyrite, pyrrhotite, marcasite, and chalcopyrite. Pyrite is widely distributed, both geologically and geographically, as it is found in rock of all types and ages. It occurs abundantly in veins, in dissemination deposits, and as masses along the contact of basic intrusives and sedimentary rocks. The temperature at which the deposits were formed is indicated by the minerals associated with the deposit. Pyrrhotite deposits and those associated with silicates are considered to have been formed at relatively high temperatures and great depths, whereas those associated with calcite, barite, and quartz are considered to have been formed at intermediate temperatures and moderate depths. The world's largest sources of pyrite have been the Alentejo region in Portugal and the Province of Huelva in Spain. Other important deposits are found in Canada, Cyprus, France, West Germany, Italy, Japan, Norway, and the United States.

Mining

Almost all the native sulfur being produced in the United States is mined by the Frasch hot-water process from salt dome deposits. Small quantities are mined by open pit from near surface deposits.

Frasch Process

The idea behind the Frasch process is extremely simple, namely, that hot water under pressure pumped through a drill hole from the surface can melt sulfur in place so that it can be carried to the surface by compressed air. In practice, the process is more difficult and has been applied successfully to only a few deposits. Of the 230 or more salt domes known in Louisiana and Texas, only 22 have been producers of sulfur of which 10 were active in 1963. To be minable by the process, the formation must have some porosity to permit entrance of hot water, but the enclosing structure must be able to restrict the molten sulfur and water from being lost to the surrounding ground.

In the development of the mine, wells are drilled through the sulfur zone to barren anhydrite below. Mining depths have ranged from 400 to 3,000 feet in the United States. The wells are drilled with a rotary rig, similar to those used in the petroleum industry for work in soft formations, and are equipped with concentric pipes ranging in size from 1 to 8 inches in diameter. A typical installation may have a 6-inch pipe to the barren anhydrite. This pipe has two sets of circumferential holes near the bottom which are separated by an internal collar. A 3-inch pipe placed inside the 6-inch pipe rests on the collar near the bottom of the sulfur formation. The collar seals the annular space between the two pipes. The 1-inch pipe inside the 3-inch pipe reaches nearly to the collar.

The water is 325° to 340° F at the plant, but this is reduced to 320° to 325° F in the field. Control of the water temperature is important because although the water should be as hot as possible for heat transfer reasons, above 318° F the viscosity increases suddenly causing sulfur removal problems. The volume of water per ton of sulfur recovered ranges from less than 1,500 gallons per ton in a highly efficient mine; 1,500 to 3,000 gallons per ton in many mines now in operation; and 4,000 to 7,000 gallons per ton in a lean, less favorable deposit. Pumps used may supply water at 250 to 350 pounds per square inch gage, but water at 125 to 200 pounds per square inch gage is normally used at the wells. The depth of the well, the length of the surface line, the porosity of the sulfur-bearing formation, and the volume of water used are related to the pressure needed. The water is transported to the ore horizon between the 6-inch and 3-inch pipes and enters the sulfur formation through the upper set of holes above the collar. The liquid sulfur, being heavier than water, settles to the bottom around the 6-inch pipe. Liquid sulfur enters the 6-inch pipe through the lower set of holes below the collar and is forced into the space between the 3-inch and 1-inch pipes by dome pressure. Compressed air entering the liquid sulfur through the 1-inch pipe decreases the density and the column rises to the surface. Air compressors delivering pressures of 500 to 600 pounds per square inch gage to the mine are used. The depth of the well, the length of air line, and the pumping rate cause pressure variations from one well to another. It requires from 500 to 900 cubic feet of air to mine a long ton of sulfur. Bleeder wells are used to remove cool water to make room for hot water being piped into the dome.

Liquid sulfur reaching the surface is discharged into steam-heated tanks at relay stations. The same relay stations also conduct the

flow of air and water to the wells. After being metered, the sulfur is pumped through steam-heated lines to storage vats, where it cools and solidifies or to liquid storage tanks. Shipments of either solid or liquid sulfur can be made by rail, road, inland waterways, or ocean. Deliveries of sulfur to U.S. markets in 1963 were 85 percent in liquid form.

The removal of large quantities of sulfur from the cap rock may affect production in two ways: (1) The formation of voids and cavities may increase the water-to-sulfur ratio and thereby increase the cost of production and (2) subsidence may distort or break the strings of pipe in the well and surface installations in the immediate area.

To reduce hot-water requirements, voids and crevices are sometimes filled by mudding. When the cavity traversed by fluid mud is large, the velocity of the fluid is decreased and solid particles settle out. In areas of low porosity the velocity is high and the solid particles tend to remain in suspension. By varying the size, percentage, and character of the solid particles in the mud, the depth of discharge, and the rate of pumping, adjustment may be made in mudflow to suit local conditions.

Subsidence resulting from the removal of large qualtities of sulfur occurs when the remaining skeleton formation does not support the weight of the overlying formations. Although collapse of this structure is disadvantageous as it may damage producing wells, it is advantageous in that it fills voids, thereby eliminating the necessity for mudding. As water circulates through the caved area with difficulty, the incoming hot water is more closely confined to the unexhausted parts of the deposit.

When sulfur is discolored by hydrocarbons, it may be treated to brighten its color; but this treatment is not necessary to permit its use for acid manufacture or for many other applications. Of the 12 active Frasch sulfur mines in the United States and Mexico, only 3—Boling, Long Point, and Ochard domes—produce bright sulfur. Freshly mined U.S. bright sulfur contains less than 0.005 weight-percent ash. Dark sulfur, although having approximately the same ash content, includes small quantities of hydrocarbons. Hydrocarbons may be removed by treating the liquid sulfur by various means. The producers have developed proprietary processes for hydrocarbon removal.

Shallow Native-Sulfur Mines

Small native-sulfur deposits are found in several Western States, including California, Colorado, Nevada, New Mexico, Utah, and Wyoming. These have been mined from time to time since 1865 in small tonnages for local use. The largest production has been from the Leviathan mine of the Anaconda Co. in Alpine County, Calif. The deposit was developed to produce sulfur to make sulfuric acid for Anaconda's Yerington, Nev., copper oxide leaching plant. Other sulfur-producing counties in California have been Alpine, Colusa, Imperial, Inyo, and Kern. In Nevada, the Western Sulphur Corp., was operating mines and plant at the Rabbitt Hole sulfur deposits, 29 miles northwest of Humboldt House (*5*).

Deposits of sulfur ore of surficial and fumerale origin or resulting from oxidation of pyrite or sulfide ores of copper, lead, and zinc are known in Colorado, New Mexico, Utah, and Wyoming.

While development efforts have been made on several of these deposits, no tonnage of any consequence was ever mined.

Recovered Sulfur

Sulfur production from sour natural and refinery gases is becoming increasingly important in supplying world sulfur needs. Production in the United States grew from 399,000 long tons in 1955 to 950,000 long tons in 1963. During the same period world production grew from 925,000 to 4.1 million tons. Canada and France became major producers of sulfur during this period and most of this production was from sour natural gas.

Important sources of sour gas occur in the Permian Basin in New Mexico, Texas, Arkansas and Wyoming; in Alberta and British Columbia, Canada; and in the Lacq area of France. Typical hydrogen sulfide (H_2S) content of sour gas in Wyoming gasfields range from 0.5 to 42 percent H_2S. The hydrogen sulfide content of gas in the Permian Basin fields was less than 2 percent with the exception of the McElroy field in Texas with 7.1 percent (*6*).

The recovery of elemental sulfur from sour natural gas and refinery gas has been very successful. Removal of the hydrogen sulfide from natural and refinery gases provides sulfur needed by the petroleum industry, sweetens the fuel gas, and reduces air pollution. The last is important near large cities where air pollution has become a civic problem.

Other industrial gases, principally from coal-burning operations, are less promising sources of sulfur supply, although their total volume is large. They are usually too lean or locally too small in quantity for economic recovery. However, considerations of air-pollution control may force the removal of sulfur oxides from

stack gases in some urban areas. In these instances, recovery of sulfur as an adjunct to the process renders the economics of removal more attractive; thus, additional supplies of sulfur become available from the consumption of high-sulfur fuels (*3*). Additionally, in certain large installations such as coal-carbonization plants, moderate quantities of sulfur are obtained.

Several processes have been developed for recovering sulfur, hydrogen sulfide, and sulfur dioxide from sour natural, refinery, smelter, and other industrial gases.

Dry processes used for removing hydrogen sulfide from gas and recovering it in the elemental form include the iron oxide process and the activated-carbon catalytic process. The iron oxide is the only dry process that has been used extensively in the United States. This process is used by utility companies for purifying coal and carburated gases and to remove the last 10 to 25 grains of H_2S per 100 cubic feet of gas following treatment by Thylox and other liquid purification processes (*18*).

In the iron oxide process, gas and air are passed downward through a series of trays containing wood shavings impregnated with iron oxide mounted within a pressure vessel. The oxygen added to the gas reacts with the ferric sulfide formed, yielding iron oxide and elemental sulfur. Disadvantages inherent to this process include intermittent operation, cumbersome equipment, high operating costs when used to remove large quantities of H_2S, and disposal problems. Offsetting these disadvantages is the ability of the process to remove H_2S to extremely low levels, at low pressures, and its selectivity for absorbing H_2S in the presence of carbon dioxide.

Wet processes, in which hydrogen sulfide is removed from a gas stream by scrubbing, utilize solutions that absorb the H_2S. The major differences in these processes are the solutions used.

In the absorber the lean solution passes downward from the top of the tower countercurrent to the upward flow of hydrogen sulfide-bearing gas. The rich solution containing the H_2S flows out of the bottom of the absorber to the top of the reactivator.

In the reactivator the rich solution passes downward from the top of the tower countercurrent to the upward flow of steam. The H_2S and steam leave the top of the reactivator and go to a steam condenser. The lean solution leaves the bottom of the reactivator and returns to the top of the absorber after cooling.

The Girbotol process is widely used for removing hydrogen sulfide and carbon dioxide from gaseous mixtures (*4, 15, 16, 21*). Various modifications of the Girbotol process permit gas purification to a degree comparable with that obtained through the use of the iron oxide process. To remove H_2S this process uses the mono-, di-, tri-ethanolamines, which are stable and relatively nonvolatile. Triethanolamine has largely been replaced by more reactive monoethanolamine for purifying natural gas, except where selective hydrogen sulfide removal is required. Diethanolamine is widely used for removing hydrogen sulfide from refinery gases.

The Shell phosphate process is a regenerative liquid purification system used for the removal and recovery of H_2S from sour natural or refinery gases and liquid hydrocarbons (*11, 17*). This process differs from the other regenerative liquid purification systems in that it employs an aqueous solution of tripotassium phosphate.

The vacuum carbonate, alkazid, and phenolate processes follow the same basic flow scheme but differ in the absorbent solutions used for recovering H_2S.

Many processes have been developed for recovering sulfur dioxide from the roasting and smelting of sulfide and sulfate ores, the refining of petroleum, and the burning of coal at power stations. Processes used to recover sulfur compounds include American Smelting & Refining Co.'s sulfur dioxide process, which recovers sulfur dioxide by use of a dimethylaniline absorber (*7*), the ammonia process (Consolidated Mining & Smelting Co. of Canada, Ltd., Trail British Columbia), the Imperial Chemical Industries basic aluminum sulfate process, the Fulham-Simon-Carves ammonia liquor process, the Orkla process, and the anhydrite process.

The principal process used for recovering elemental sulfur from H_2S is the modified Claus (*1*). In the original process developed by Claus, H_2S was admixed with air and burned in a large combustion chamber containing a ferric oxide catalyst. Owing to the large quantity of heat liberated, the operating temperatures were extremely high, resulting in only partial conversion of hydrogen sulfide to sulfur.

Two modified Claus processes are in general use today. In the one, the partial-combustion process, the acid gas is burned in a combustion furnace with sufficient air to convert all of the hydrogen sulfide to sulfur according to the following stoichiometric equation:

$$2H_2S + O_2 \rightarrow (2/x)S_x + 2H_2O.$$

The term "partial combustion" is derived from the fact that the air required by the above equation is sufficient to convert only one-third of the hydrogen sulfide to sulfur dioxide. Both unconverted hydrogen sulfide and sulfur dioxide

emerge from the reaction furnace in the gas stream along with sulfur vapor and are themselves converted to elemental sulfur in catalytic converters which follow.

In the other, the split-stream process, one-third of the hydrogen sulfide is burned completely to sulfur dioxide in a combustion furnace according to the following stoichiometric equation:

$$2H_2S+3O_2 \rightarrow 2SO_2+2H_2O.$$

The combustion gases are mixed with the other two-thirds of the hydrogen sulfide so that the following catalyzed reaction may take place:

$$2H_2S+SO_2 \rightarrow 2H_2O+(3/x)S_x.$$

The yield of sulfur, or the total conversion of H_2S to sulfur, is influenced by the amount of water vapor, the temperature in the final catalytic converter, the concentration of H_2S in the acid gas, the pressure used, the presence of hydrocarbons, and the catalyst. Modern, properly operating sulfur plants ordinarily obtain conversions between 90 and 95 percent.

USES

In utilizing sulfur at least 91 percent passes through the sulfur dioxide stage. Sulfur end uses are so varied that the consumption of sulfur is often taken as a reliable indicator of industrial activity. The major groups of uses are given in table 1 (*10*).

TABLE 1.—*Sulfur consumption by industry*

	Percent
Acid (sulfuric):	
Fertilizers (superphosphate and ammonium sulphate)	40
Chemicals	20
Petroleum	2
Pigments	8
Steel	4
Rayon and film	4
Other	7
Total acid	85
All other uses:	
Sulfite pulp	6
Carbon bisulfide	3
Ground and refined	3
Other	3
Total other uses	15

A partial list of products produced using sulfur or sulfuric acid given below indicates the widespread industrial dependence on sulfur:

Acids
Alcohols
Alum
Ammonium sulfate
Analine
Bleaching agent
Bromine
Carbon dioxide
Carbon disulfide
Carbon tetrachloride
Casein
Caustic soda
Cellophane
Celluloid
Cellulose esters
Cements
Chlorine
Coke
Copper
Dehydrating agent
Detergents
Dyes
Ebonite
Electroplating
Explosives
Fertilizers
Fire extinguishers
Fireproofing agents
Fireworks
Food preservatives
Fumigants
Fungicides
Glue
Glycerin
Impregnant
Inorganic or organic acids
Insecticides
Leather
Livestock food
Lubricants
Magnesium
Matches
Medicine
Metallurgy
Paints and pigments
Paper pulp
Petroleum products
Pharmaceuticals
Phenol
Photography
Plastics
Plate glass
Rayon
Refrigerants
Resins
Road-surfacing materials
Rubber goods
Soap
Soda
Solvents
Steel pickling and galvanizing
Storage batteries
Sugar
Sulphonated oils
Synthetic fibers
Synthetic rubber
Textiles
Tires and rubber
Water purification

A rapidly changing technology has created new sulfur demands and made others obsolete. Since sulfuric acid is an active acid well below the cost of other acids of comparable activity it is tried first in most research requiring acid. During the 1940's aviation gasoline, synthetic ammonium sulfate, ethyl acohol, and synthetic detergents became important sulfuric acid consuming industries. However, the salt-sulfuric acid process for manufacturing hydrochloric acid was displaced by byproduct recovery hydrochloric acid from organic chlorination. In the 1950's new markets were developed in processing uranium, ammonium phosphates, tall oil, and DDT, but the industrial explosives market was lost to ammonium nitrate.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Elemental sulfur and sulfuric acid are recovered as byproducts at smelters treating copper, lead, and zinc sulfide ores.

Elemental sulfur and hydrogen sulfide are recovered as byproducts in the treatment of sour natural, refinery, and other industrial gases.

Iron sinter is recovered as a coproduct in manufacturing sulfuric acid from pyritic ores.

Pyrites can be recovered as byproducts at coal-washing plants. Sulfur compounds leached from coal mines and waste dumps may contribute to stream pollution.

Cement is recovered as a coproduct in the production of sulfuric acid from anhydrite.

ALTERNATE MATERIALS

Substitutes for sulfur or sulfuric acid have been developed for only a small part of total consumption. Hydrofluoric acid may be used instead of sulfuric acid in manufacturing high-octane gasoline. Nitric acid, at a cost, could be used by the fertilizer industry where the introduction of sulfur is not required. Hydrochloric acid could be used for steel pickling. For many years the ample supply and low price of sulfur have restricted the use of alternates.

RESERVES

Reserves of sulfur and sulfur-bearing material in the United States and the rest of the world are ample to supply any probable demand, and an orderly transition can be made to alternate sources of sulfur as supplies of low-cost sulfur are depleted.

It is unlikely that any more onshore salt-dome deposits will be discovered on the gulf coast, although numerous salt-dome deposits occur offshore within 40 miles of the coast of Louisiana and Texas. One sulfur deposit in the Gulf of Mexico is being utilized and one more is known. Reserves of native sulfur recoverable by the Frasch process have been estimated to range from 50 to almost 200 million tons. Since not all the domes in the Gulf of Mexico have been explored, and since Boling dome of Texas Gulf Sulphur Co. has already yielded over 50 million tons of native sulfur, potential resources of native sulfur in the Gulf coast area might exceed 200 million tons (*12*). The salt domes being exploited in Mexico have been estimated to contain more than 50 million tons of native sulfur.

Surface deposits are unlikely to contain as much as 30 million tons.

Sulfides, other than in coal, contain from 100 million to 150 million tons of sulfur.

Sulfur in coal is the second largest reserve of this element. Some pyrites in coal can be recovered by present methods. Finely disseminated pyrite is too difficult to recover by physical means. The sulfur from finely disseminated pyrite in coal and the organic sulfur content is expected to be recoverable only from flue gases. The sulfur content of various coals in the United States normally ranges from 2 to 3 percent. Coal in minable deposits may contain as much as 5 billion tons of sulfur.

Sulfates contain more sulfur than all other reserves combined. The quantity of sulfur in gypsum, anhydrite, and as sulfates in sea water is tremendous.

The probable sulfur in known recoverable reserves of fossil fuels can be calculated from published quantity data (*20*). Assuming that minable coal contains 2.6 percent total sulfur, petroleum contains 0.6 percent sulfur, shale oil contains 0.75 percent sulfur, and natural gas averages 0.05 percent sulfur, there is 5.1 billion tons of sulfur in known recoverable fossil fuels in the United States.

Probable sulfur reserves in the United States can be summarized as follows:

Source:	*Sulfur (million long tons)*
Salt dome deposits	200.
Surface deposits	10–30.
Sulfide ores	100–150.
Coal	5,000.
Petroleum	45.
Natural gas	7.
Shale oil	50.
Anhydrite and gypsum	Enormous.
Sea water	Enormous.

Pyrites are the most abundant of the metalliferous minerals and occur in ores of great variety and number. Pyrite (FeS_2), the commonest type, is present in small quantities in many igneous and sedimentary rocks. Only occasionally is it found in sufficient quantities and pure enough to be of commercial value. Large pyrites deposits, principally pyrrhotite, occur along the Appalachian belt in St. Louis County, N.Y.; Louisa County, Va.; Great Gossan Lead, Va.; and Ducktown, Tenn. Other large deposits are found in Bingham, Utah; Shasta County, Calif.; Jerome, Ariz.; and Maine. Smaller deposits of pyrites occur in Georgia, Missouri, Pennsylvania, South Carolina, Wisconsin, South Dakota, Colorado, Arizona, Montana, and Vermont. Large quantities of pyrites are found in slates and schists in the iron districts of Iron River, Mich., and Cuyuna, Minn.

Although the reserve of pyrites in byproduct sources is large, it becomes available slowly in quantities determined by the rate at which the main product is produced. Mine dump and tailing basins at some of the older mining properties are available sources of pyrites. Additional tonnages are constantly being added at these and other mining properties as mining progresses.

The large quantity of sulfur dioxide released in the smelting of the sulfide ores of copper, lead, zinc, and nickel is potentially a much larger source of sulfur or sulfuric acid than at present, but this source must be discounted in part owing to various physical and economic factors. Frequently, the sulfur dioxide gas produced at smelters is too dilute to be used as a satisfactory feed for an acid plant unless enriched by other means. Most smelters are situated in remote areas; consequently, transportation costs to acid markets are prohibitive.

There are many principal reserves of sulfur in addition to those in the United States and the Frasch reserves in Mexico. For example

there are large reserves of sulfur recoverable from natural gas in Canada, France, and elsewhere; there are possibly 100 million tons of volcanic sulfur in the Andes and perhaps 25 to 50 million tons in Japan; and the Tarnobrzeg deposit in Poland has a measured reserve of 90 million tons.

SOURCES OF STATISTICAL INFORMATION

Annual and monthly data on the production, shipment, and stocks of sulfur in the United States are obtained from producers by the Bureau of Mines. World production data are compiled by the Bureau from foreign service dispatches and official publications of foreign countries, and figures on foreign trade are obtained from the Bureau of the Census. Selected special information is obtained by contacting sulfur producers and distributors.

PRODUCTION, CONSUMPTION, AND TRADE

In 1963 the United States supplied about 60 percent of the world production of native sulfur, 46 percent of the elemental sulfur (including native), and 4 percent of the world pyrite production.

The production of sulfur and sulfur-containing raw materials in the United States and the world production of elemental sulfur by countries are shown in tables 2 and 3, respectively.

The United States is the world's largest consumer of sulfur. Consumption was 34 percent of the free world total in 1963. This was an alltime high.

Imports of elemental sulfur from Mexico and Canada increased rapidly in the last few years and reached 863,000 tons and 480,000 tons, respectively, in 1963. The development of large-scale sulfur production in Mexico, Canada, and France since 1956 changed the foreign trade patterns with the United States losing some markets in these and other countries but gaining new markets elsewhere. Imports and exports are shown in table 4. Imports of pyrites are shown in table 5.

Most of the sulfur exported from the United States is the so-called crude run-of-mine Frasch sulfur (99.5 percent pure) from Texas and Louisiana. Sulfur was also exported in the crushed, ground, refined, sublimed, and flowers forms. In 1963 major exports went to India, 16 percent; the United Kingdom, 15 percent; Canada, 9 percent; Brazil, 8 percent; and Australia, 8 percent.

Transocean shipments of sulfur were all in solid form until May 1964 when liquid-sulfur deliveries to Rotterdam, Netherlands, were started.

The United States does not levy a tariff on sulfur.

STRATEGIC CONSIDERATIONS

The United States continues to be self-sufficient in sulfur and has a surplus of elemental sulfur for export. In addition, Canada and Mexico are two of the world's largest producers and both are growing in sulfur production capacity. Recovered sulfur from domestic sour natural and refinery gas and imports from Canada and Mexico have been growing and have satisfied increased domestic needs while Frasch production has remained stable. Frasch reserves are adequate for the foreseeable future.

Sulfur is not stockpiled by the Government, but producers' stocks of Frasch and recovered sulfur could satisfy domestic needs for 9 months at the 1963 rate of demand.

Because the Frasch sulfur industry is concentrated in the Gulf Coast States of Texas and Louisiana and on the Isthmus of Tehuantepec in Mexico shipping sulfur by the usual maritime routes makes it vulnerable to submarine attack. Inland shipments by barge and recovered sulfur from scattered producers in the United States and Canada shipped by rail would be less vulnerable.

PRICES

The price of sulfur has remained relatively stable over a long period of time because of the inelastic nature of demand. Posted prices have differed from contract prices with the latter containing a competitive allowance as required by current marketing conditions. Prices have changed somewhat in the last few years as a result of the development of liquid sulfur deliveries to consumers in the United States and to oversea markets. Delivered prices from regional liquid-sulfur terminals include transportation, handling, and storage costs.

Historically, posted prices remained at $18 per long ton, f.o.b. mines, from 1926 to 1938. Prices dropped to $16 for the period 1938–47; rose to $18 for 1947–50; and rose to $21 to $22 in 1950. The Office of Price Stabilization froze the price of sulfur at $21 to $24 per long ton f.o.b. mine for domestic sales in 1951. Export prices were $25 to $27 per long ton f.o.b. port. Price controls were removed on March 17, 1953. Prices rose to $25.50 to $27.50 f.o.b. mines for domestic sales and $28 to $30.50 f.o.b. port for export. Domestic prices remained at this level until 1957 when prices were reduced $3 per ton

to $23.50 and $22.50 per long ton f.o.b. mines for bright and dark sulfur, respectively, when competition from Mexican Frasch sulfur began. Export prices were $25 and $24 f.o.b. port for bright and dark sulfur, respectively. In 1959 Freeport Sulphur Co. initiated a $3.50-per-ton competitive allowance for water shipments to east coast ports and a $1 per ton discount for barge shipments on the Mississippi River and other inland waterways but posted prices remained unchanged. In 1961 competitive allowances along the east coast of the United States were reduced to adjust for a $2-per-ton increase in price of Mexican Frasch sulfur in these markets. In 1961 prices along the east coast and the oversea markets increased. In 1962 a competitive allowance of $1.50 to $3 to the upper Midwest was provided to offset competition from increasing Canadian sulfur imports.

TABLE 2.—*Production of sulfur and sulfur-containing raw materials by producers in the United States*

[Long tons]

	Gross weight	Sulfur content	Gross weight	Sulfur content	Gross weight	Sulfur content
	1954–58 (average)		1959		1960	
Native sulfur or sulfur ore:						
Frasch-process mines	5,562,391	5,562,391	4,553,634	4,553,634	4,942,935	4,942,935
Other mines	181,938	55,057	331,237	86,182	379,067	94,357
Total		5,617,448		4,639,816		5,037,292
Recovered elemental sulfur:						
Brimstone	476,507	474,554	688,487	686,407	769,319	766,566
Paste	281	129				
Total		474,683		686,407		766,566
Pyrites (including coal brasses)	1,005,414	417,242	1,056,617	436,871	1,016,263	416,213
Byproduct sulfuric acid (basis—100 percent) produced at Cu, Zn, and Pb plants	1,028,868	336,250	969,678	316,600	1,056,890	345,075
Other byproduct sulfur compounds [1]	100,474	87,406	104,887	88,046	114,359	95,395
Total		6,933,029		6,167,740		6,660,541
	1961		1962		1963	
Native sulfur or sulfur ore:						
Frasch-process mines	5,385,468	5,385,468	4,984,578	4,984,578	4,881,512	4,881,512
Other mines	400,015	92,025	162,186	40,840	1,371	415
Total		5,477,493		5,025,418		4,881,927
Recovered elemental sulfur:						
Brimstone	861,413	858,169	902,124	899,598	949,567	946,753
Paste						
Total		858,169		899,598		946,753
Pyrites (including coal brasses)	987,309	398,519	915,890	379,046	824,800	343,566
Byproduct sulfuric acid (basis—100 percent) produced at Cu, Zn, and Pb plants	1,016,731	331,963	1,088,397	355,362	1,089,523	355,730
Other byproduct sulfur compounds [1]	126,923	106,335	115,670	97,787	136,509	115,826
Total		7,172,479		6,757,211		6,643,802

[1] Hydrogen sulfide and liquid sulfur dioxide. In addition, a quantity of acid sludge is converted to H_2SO_4 but it is excluded from the above figures.

TABLE 3.—*World production of elemental sulfur by countries* [1] [2]

[Long tons]

Country	1959	1960	1961	1962	1963
Native sulfur:					
Frasch:					
Mexico	1,293,181	1,261,574	1,148,494	1,350,375	1,456,656
United States	4,553,634	4,942,935	5,385,468	4,984,578	4,881,512
Total	5,846,815	6,204,509	6,533,962	6,334,953	6,338,168
From sulfur ores:					
Argentina	25,207	39,265	22,183	22,303	[3] 22,300
Bolivia (exports)		1,175	4,896	7,247	9,793
Canary Islands	2,900	3,900	4,900	5,900	[3] 5,900
Chile	21,676	30,900	43,994	54,132	57,000
China [3]	100,000	120,000	120,000	120,000	120,000
Colombia	8,824	8,899	9,941	10,046	[3] 10,000
Italy	116,252	79,703	68,668	53,068	41,128
Japan [4]	215,669	243,684	238,456	220,438	217,998
Mexico	[3] 17,700	[3] 17,700	25,116	26,751	28,968
Philippines		43	158	926	47
Poland	10,500	25,000	227,000	337,000	303,300
Spain	2,851	1,336			
Taiwan	5,533	5,725	5,472	7,462	7,144
Turkey	13,174	16,830	15,506	18,247	19,123
U.S.S.R. [3]	600,000	800,000	900,000	950,000	950,000
United Arab Republic (Egypt)	1,200	3,500	9,000	[3] 6,000	4,675
United States	86,182	94,357	92,025	40,840	415
Total [3] [5]	1,230,000	1,490,000	1,790,000	1,880,000	1,800,000
Total native sulfur	7,075,000	7,700,000	8,320,000	8,220,000	8,140,000
Other elemental:					
Recovered:					
Bulgaria [6]	4,000	5,000	5,000	6,000	[3] 6,000
Canada (sales) [7]	130,050	244,963	352,466	620,623	1,037,190
China [3] [6]	100,000	120,000	120,000	120,000	120,000
Finland					50,000
France [8]	419,273	778,157	1,080,013	1,326,000	1,396,000
Germany:					
East	106,153	100,130	115,000	118,000	[3] 118,000
West	78,474	82,807	82,861	90,666	[3] 85,000
Iran [3] [9]	19,000	20,000	20,000	15,000	20,000
Italy [3]	4,000	3,200	2,000	2,000	2,000
Japan [9]	7,829	8,326	8,163	8,549	11,429
Mexico [8]	45,054	33,487	51,086	46,545	43,308
Netherlands [6]	30,700	30,000	38,000	28,000	33,000
Netherlands Antilles: Aruba and Curacao [3]	30,000	40,000	40,000	40,000	30,000
Norway [6]	77,111	71,256	61,156	45,175	
Portugal [6]	15,888	10,915	8,813	6,637	3,000
South Africa, Republic of [9]			2,163	1,913	1,981
Spain [6]	25,719	40,194	48,323	41,836	27,519
Sweden [10]	37,576	38,900	30,500	[3] 30,000	25,000
Taiwan [9]	810	875	1,968	2,130	2,310
Trinidad [3] [9]	5,000	5,000	5,000	5,000	7,000
U.S.S.R. [3]	180,000	210,000	275,000	370,000	400,000
United Arab Republic (Egypt)	2,403	2,345	2,545	2,039	[3] 3,000
United Kingdom [11]	53,173	62,402	58,405	51,900	45,000
United States	686,407	766,566	858,169	899,598	946,753
Total other elemental	2,060,000	2,675,000	3,270,000	3,880,000	4,415,000
World total (estimate) [2]	9,135,000	10,375,000	11,590,000	12,100,000	12,560,000

[1] This table incorporates some revisions.
[2] Data do not add exactly to totals shown because of rounding where estimated figures are included in the detail.
[3] Estimate.
[4] Includes sulfur from mixed sulfur-sulfide ore.
[5] In some years Iran produces mine sulfur equivalent to 250–1,500 tons of sulfur. No estimates in total.
[6] From sulfide ore.
[7] Produced from natural gas, includes a small quantity derived from treatment of nickel-sulfide matter at Port Colborne, Ontario.
[8] From natural gas.
[9] From refinery gases.
[10] From shale oil.
[11] Including sulfur recovered from petroleum refineries.

TABLE 4.—*U.S. imports for consumption and exports of sulfur*

Year	Imports		Exports			
			Crude		Crushed, ground, refined, sublimed and flowers	
	Long tons	Value (thousands)	Long tons	Value (thousands)	Long tons	Value (thousands)
1954–58 (average)	267,631	[1] $6,407	1,610,707	$46,164	$25,536	$1,957
1959	642,488	13,901	1,612,158	39,975	23,449	2,025
1960	741,370	15,453	1,775,526	40,880	11,017	1,413
1961	831,517	17,152	1,585,531	35,370	10,512	1,254
1962	1,040,473	20,310	1,537,419	35,496	16,567	1,799
1963	1,351,216	23,942	1,603,438	33,531	9,199	1,057

[1] Data known to be not comparable with other years.

Source: Bureau of the Census.

In 1964 price increases on new business came first in the oversea markets. A domestic price increase of $2 per ton became effective on new business on July 1 and as of January 1, 1965, on business under contract. Published prices at beginning January 1, 1965, were $27.50 per long ton f.o.b. gulf ports for bright sulfur to be exported; $25.50 per long ton f.o.b. mines and $27 per long ton f.o.b. gulf ports for domestic markets. The published price for acid grade or dark sulfur at any point or for any market was $1 less than that for bright sulfur.

The Mexican Frasch producers, Pan American Sulphur Co. and Gulf Sulphur Co., increased prices $2 per long ton to all markets.

TAXES

The sulfur industry has the usual taxation problems faced by all industry and in some States pays severance taxes. In Texas and Louisiana, severance taxes of $1.03 a long ton are imposed. Domestic producers are granted a depletion allowance of 23 percent on income from domestic and foreign production.

TRANSPORTATION, STORAGE, AND HANDLING

In 1963, 85 percent of the elemental sulfur used in the United States was delivered to consumers in liquid form. United States and Mexican Frasch producers shipped liquid sulfur to 27 producer-controlled regional storage and transshipment terminals in 1963. The location and capacity of these terminals are listed in table 6. The terminals were supplied by tankers along the coast and by barges on inland waterways. The widespread acceptance by the U.S. consuming industry was followed by the development of liquid-sulfur service overseas. The Sulphur Export Corp. (Sulexco) which sells for the four U.S. Frasch producers overseas contracted for two oceangoing liquid-sulfur carriers of 25,000-ton capacity each and for a liquid-sulfur terminal at Rotterdam, Holland. The first liquid-sulfur delivery overseas was made by the *Naess Texas* during May 1964 to Sulexco's Rotterdam, Netherlands, terminal. A sister ship, the *Naess Louisiana*, began service in the second half of 1964 after launching in

TABLE 5.—*U.S. imports for consumption of pyrites containing more than 25 percent sulfur, by customs districts*

[Long tons unless otherwise specified]

Customs district	1954–58 (average)	1959	1960	1961	1962	1963
Buffalo	304,293	230,606	244,103	249,230	262,580	172,893
Chicago				52		
Connecticut	4	262				154
Maine and New Hampshire						133
Massachusetts					1	
Michigan	17,630	13,182	11,870	12,583	16,379	18,928
Montana and Idaho			37	14		
New York	43					
Pittsburgh	299					
Rochester	41				1	
St. Lawrence	7,899	14,640	21,338			
San Francisco					104	
Vermont	9,676	21,948	28,868	19,725	22,834	2,063
Washington	43					
Total:						
Long tons	339,928	280,638	306,216	281,604	301,899	194,171
Value	$1,197,505	$868,495	$1,075,271	$741,942	$746,744	$487,663

Source: Bureau of the Census.

TABLE 6.—*Liquid sulfur regional storage and transshipment terminals in operation* [1] *in 1963*

Producer controlled terminals	Number of storage tanks	Total storage capacity (thousand long tons)
Freeport Sulphur Co.:		
Baton Rouge, La.	1	6.5
Bucksport, Maine	2	20.0
Charleston, S.C.	1	10.0
Everett, Mass.	1	10.0
Joliet, Ill.	3	30.0
Le Moyne, Ala.[2]	2	9.8
Nitro, W. Va.	2	18.0
Tampa, Fla.	4	40.0
Tuscaloosa, Ala.[2]	1	3.8
Warners, N.J.	2	12.5
Wellsville, Ohio	2	20.0
Total	21	180.6
Gulf Sulphur Corp.:		
Baltimore, Md.	1	10.0
Tampa, Fla.	1	10.0
Total	2	20.0
Pan American Sulphur Co.:		
Baltimore, Md.	1	10.0
Newark, N.J.	1	10.0
Tampa, Fla.	3	30.0
Total	5	50.0
Texas Gulf Sulphur Co.:		
Baltimore, Md.	2	24.0
Carteret, N.J.	2	26.0
Cincinnati, Ohio	3	16.8
Jacksonville, Fla.	1	11.0
Marseilles, Ill.	1	10.0
Newell, Pa.[1]	1	10.0
Norfolk, Va.	2	20.8
Paulsboro, N.J.[1]	2	24.0
Savannah, Ga.	1	11.0
Tampa, Fla.	1	7.5
Wilmington, N.C.	1	8.0
Total	17	169.1

[1] Completed in 1963 but not in operation. [2] Began operating in 1963.

June in England. Pan American Sulphur Co. of Mexico, a Frasch producer, and the Société Nationale des Pétroles d'Aquitaine of France, a recovered-sulfur producer, built liquid-sulfur terminals at Immingham, England; Rotterdam, Netherlands; and Rouen, France.

Sulfur is an excellent heat insulator and is readily kept liquid by steam coils while in shipment or storage. If solid, the same coils can act as remelters. Advantages in using liquid sulfur include reduction in labor costs, wind losses, contaminations, and melting costs.

Liquid sulfur may be handled in iron and steel equipment if moisture is absent. Aluminum containers are satisfactory for storing liquid or dry solid at normal temperatures. Special stainless steel containers, pipes, etc., are required at elevated temperatures (above 444.6° C).

Safety considerations require the removal of hydrogen sulfide and carbon disulfide, if they occur, by ventilation to outside air. Both are potentially explosive; carbon disulfide has exploded in contact with steam pipes (*9*).

Most of the sulfur exported from the United States is crude Frasch sulfur from Texas and Louisiana. Sulfur was also exported in the crushed, ground, refined, sublimed, and flowers forms. United Kingdom, India, Canada, Brazil, Australia, and the Netherlands were the chief recipients of crude sulfur in 1963.

Freshly broken sulfur weighs approximately 84 pounds a cubic foot. This weight may be increased to 90 pounds per cubic foot after several handlings, owing to the tendency of sulfur to settle and pack. Its angle of repose is normally about 35°, although vertical faces may develop in removing sulfur from a stockpile.

The equipment used for handling bulk sulfur depends on the quantity to be moved and may range from hand shovels or wheelbarrows to power shovels or conveyor systems.

In the broken state, sulfur, particularly under humid conditions, may become corrosive; consequently, sulfur companies recommend the use of corrosion-resistant materials such as aluminum, stainless steel, rubber, and wood in conveyors, hoppers, chutes, cars, and other pieces of equipment.

Shrinkage resulting from mechanical spillage, windborne loss during transfer, and wind and rain erosion of outside storage averages about 0.5 percent, but sometimes is substantially higher.

RESEARCH

In a sense, every chemist who tries sulfuric acid first in an experiment is doing research for the sulfur industry. A search of the patent files reveals a very large number of patents dealing with sulfur or its compounds. In addition, all large producers do some research and several outside groups have been formed. The Sulphur Institute with offices in Washington, D.C., and London, England, is supported by producers of

Frasch and recovered sulfur and pyrites. It operates on a grant-in-aid basis in the United States, Europe, Australia, and New Zealand. The research is done in universities or by industrial groups. The Institute distributes literature in the field of interest. Primary interest is on agricultural uses for sulfur. Freeport Sulphur Co. opened a central Research and Development Laboratory at Belle Chasse, La., in 1962. Its research includes increasing the knowledge of the manufacture of sulfuric acid among other things. Texas Gulf Sulphur Co. recently published a sulfur manual.

In Canada, two groups are active, the Research Council of Alberta and a newly formed group, the Alberta Sulphur Research, Ltd.

Several reports by the Bureau of Mines have been issued or are nearing completion on the sulfur industries of regional areas of the United States.

OUTLOOK

World demand for sulfur is expected to grow as underdeveloped countries become industrialized, and the production of sulfuric acid for fertilizer manufacture is increased to reduce food shortages. By 1970, consumption of sulfur in all forms may be 25 million long tons per year of which 15 million tons is expected to be elemental.

The dependence on U.S. Frasch sulfur has been reduced by the rapid development of sulfur industries in Mexico, Canada, and France. Mexican Frasch capacity is being increased from 1.9 to 2.5 million tons per year while Canada, prior to 1964, did not use fully her 1.9-million-ton capacity. Larger Canadian capacity is expected, but this is related to sales of natural gas using pipelines not yet authorized or constructed. French production presently uses all of a 1.45-million-ton-per-year capacity and sales are not expected to increase because of the planned rate of production of natural gas. Poland is planning to produce 1.0 million tons of sulphur per year from the Machow deposits by open-pit mining by 1975.

U.S. Frasch production has remained relatively stable and will grow by utilizing full capacity of present mines and opening new ones as demand exceeds supply. Offshore sulfur deposits offer the best promise of new reserves. Frasch potential resources should last until the year 2000 at the present rate of production. Recovered sulfur from sour natural and refinery gas will become an increasing important source of sulfur in the United States. Development of the huge Athabasca oil sand deposits in Alberta, Canada, may eventually contribute large tonnages, but only 200,000 tons per year is forecast for 1970. Ultimately, greater use will need to be made of pyrite and gypsum as sources of sulfur, but greatly expanded use of sulfur in smelter gases is not predicted in the United States in the near future, and it will be a long time before gypsum and anhydrite will be sources of domestic sulfur.

Elemental sulfur sold in the United States is now 85 percent in liquid form. Movement overseas of liquid sulfur is developing and will increase, but most oversea deliveries will be solid sulfur.

Sales groups, such as the Sulphur Export Corp. (Sulexco) of the United States, and Cansulex of Canada will expand foreign markets. Sulfur utilization research should become more intense and will ultimately be a factor in increasing sales.

Prices, historically quite stable, will increase and may approach the peak prices of 1956. Price increases will bring about the development of additional reserves.

More sulfur may be recovered from sulfur-bearing gases produced at metallurgical plants, but this source will not expand rapidly unless there is some major development in the recovery of elemental sulfur from hot, dilute gases.

The ratio of production of elemental sulfur to pyrites, usually fairly constant, is expected to increase.

For the foreseeable future, the North American Continent will continue to supply the major quantity of world sulfur, unless a substantial source of easily recoverable sulfur is discovered elsewhere. There does not appear to be any source that will replace Frasch sulfur in its dominant position. Production of recovered sulfur will increase and continue to supplement that produced from Frasch mines. It may be recovered from high-sulfur crude oil in the Middle East.

It has been estimated that, exclusive of by-product sulfuric acid, the demand for sulfur in the United States will be 12.5 million tons per year by 1975 (*14*).

PROBLEMS

The principal problems of the sulfur-producing industry are economic rather than technical. Technical improvements in most sulfur-producing and utilization processes will occur just as technical progress is being made in most industries.

While reserves appear to be adequate for perhaps 40 years, the present and future producers of sulfur must do sufficient exploration and development work to permit timely production from new sources. Since 11 years passed between discovery and production at Grand Isle it is apparent that offshore exploration should be 6 to 10 years ahead of production. Enough know-how and experience has been gained so additional new deposits could be brought in faster unless more difficult oceanographic conditions prevail.

Privately financed sulfur producers in the United States must compete, for both domestic and overseas markets, with sulfur from Mexico produced from mines that were subsidized during the development period and whose products may be exported to U.S. ports in ships at rates below those available for U.S. producers to ship their sulfur to the same ports.

Preferential freight rates that are available for sulfur produced in Canada and marketed in Midwestern United States creates unequal marketing problems in the industrialized north-central part of the country.

Unequal competitive practices which put U.S.-produced sulfur at an economic disadvantage in world markets could result in the closing of some Frasch mines before the maximum quantity of sulfur had been removed. This problem of conserving sulfur resources through maximum extraction would become more acute whenever sulfur prices decrease.

Trade barriers in the form of high import duties, required licenses, quotas, complete embargos, special taxes, or required deposits all make marketing of U.S.-produced sulfur more difficult to users in some countries. Long-term credit insurance is essential to the exporting of sulfur to countries where the political or economic conditions are unfavorable for prompt payment for material received.

Lack of adequate information on the location and quality of undeveloped or unknown reserves, new market areas, and costs of producing sulfur or sulfur compounds hampers development of output from local resources.

Similarly, the lack of efficient and economical processes restricts the use of non-Frasch resources and sulfur-bearing waste products of other industries. This is a limiting factor in the recovery of both primary and secondary sulfur. The hazards and nuisance situations involved in producing and handling sulfur and its compounds, especially those to be recovered from hot dilute sulfurous gases, are continuing problems to the industry.

Accurate and current statistics on the use pattern of sulfur and sulfuric acid is a serious information problem to industry and government organizations concerned with these commodities.

All sulfur producers encounter many serious individual problems in the mining and production of their products. In addition, there are numerous common problems, such as taxation, freight rates, competition with substitutes, and need for basic commodity information.

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TALC, SOAPSTONE, AND PYROPHYLLITE

By J. Robert Wells [1]

TALC, soapstone, and pyrophyllite are used in a multitude of ways and enter into practically every aspect of modern living, although no more than a small fraction of the total quantity used appears in such easily recognized forms as marking crayons or toilet powders. A much greater amount, over 90 percent of the total U.S. consumption, finds its way into ceramics, paints, fillers, and refractories.

The earliest recorded uses of soapstone were for carved ornaments, building stone, and cooking utensils. Ground talc was first produced in New York in 1880, and since that year New York consistently has produced more talc than any other State. In recent years North Carolina and California have also been major producers of talc and pyrophyllite.

Deposits occur in many States and in most foreign countries; the greatest production usually comes from those areas where industrial development is greatest. The United States produces about 25 percent of the world total. Since 1930 the value of talc, soapstone, and pyrophyllite consumed annually in the United States has increased at a rate about 1½ times that of gross national product in constant dollars. Domestic production in 1963 totaled 804,000 short tons, sales were 794,000 tons valued at $18 million, and apparent domestic consumption was 763,000 tons. Strategic block talc is imported from India and Italy; high-grade ground talc is imported from India, Italy, and France. Imports have declined in recent years.

Talc, soapstone, and pyrophyllite deposits are believed to have been formed during periods of intense dynamic disturbance through hydrothermal alteration or contact metamorphism of preexisting rocks. The whiter, purer talcs were derived from sedimentary magnesium carbonate rocks, the less pure from ultrabasic igneous rocks, and pyrophyllite from acidic igneous rocks.

The physical and chemical properties of talc vary with its genesis, and its uses often depend on specific properties. Talcs from different deposits are not always interchangeable in industrial applications. Although few, if any, minerals surpass talc in multiplicity of uses, the ceramic, paint, rubber, insecticide, roofing, and paper industries consumed 79 percent of the 1963 output of talc and soapstone. The remainder was used in toilet preparations, asphalt filler, foundry facings, refractories, and a large number of minor applications.

The United States is self-sufficient in all grades of talc, soapstone, and pyrophyllite except block steatite talc and block pyrophyllite, the requirements for which are small. Block steatite talc is on the list of strategic and critical materials for stockpiling, but phosphate-bonded talc is a satisfactory substitute. In an emergency, conversion to the phosphate-bonded material could be accomplished quickly.

Except for industrial research to control quality and expand the uses of these commodities, little money or time is expended on research. Some work was done by the National Bureau of Standards on talc synthesis. The Bureau of Mines and others have conducted beneficiation research on talc and pyrophyllite and on the chemical bonding of ground steatite talc.

The short- and long-term supply outlook for talc, soapstone, and pyrophyllite is good, and consumption should continue to increase at a rate greater than that of the gross national product.

There is need for additional research to find new uses for the plentiful grades of talc, soapstone, and pyrophyllite, to lower mining and processing costs, and to improve quality.

[1] Commodity specialist.

BACKGROUND

The earliest known uses of soapstone, which depended upon the ease with which it could be cut, were for amulets, and building stone.

Soapstone was first used on this continent by the American Indians, who early availed themselves of its heat-retaining and easy cutting qualities for making bowls, pots, cooking stoves, and other utensils. These uses suggested the term "potstone," which is still applied to soapstone in some localities. The early European settlers on the North American Continent used heated blocks of cut soapstone extensively as warming stones in carriages, sleighs, and beds, a practice that survived until recent times. Beginning between 1870 and 1880, tubs, sinks, hearthstones, mantels, fireless cookers, griddles, firebrick, and various utensils were manufactured from soapstone. The first talc grinding mill was established at Gouverneur, N.Y., about 1880, and the product was used principally for paper filler (*1*).[2]

From 1880 to 1900, inclusive, the annual output of the talc and soapstone industry of the United States was about 88,000 short tons valued at about $1 million. These figures include manufactured soapstone items.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF INDUSTRY

In 1963 there were 34 talc, 12 soapstone, and 11 pyrophyllite producers. One company produced talc and pyrophyllite, and one company produced talc and soapstone; all others produced only one commodity. Operations ranged from individuals mining less than 100 tons a year of crude ore, mainly in California, to companies producing several tens of thousands of tons from either a single deposit or several deposits. In 1963 sales of talc, soapstone, and pyrophyllite in the United States totaled 794,000 tons valued at $18 million.

The larger producers were grinders of talc, soapstone, and pyrophyllite in mills either adjoining or near the deposits or at sites convenient to the major markets. All talc produced in Nevada, however, was shipped to California, part of the California and Montana output was shipped to Nebraska and Utah, and part of the Washington output was shipped to Oregon for grinding. One company in North Carolina produced talc crayons in 1963 in addition to ground material. One company in Maryland produced sawed talc for ceramic purposes in addition to crushed material.

Substantial quantities of crude ore were sold by producers to merchant grinders, especially in California. Part of the crude and prepared talc, soapstone, and pyrophyllite was sold directly to consumers by the producers; the remainder was sold to brokers. Some brokers also imported high-quality talc.

Most of the block steatite talc used for electronic tube spacers in the United States was processed by firms in Englewood, N.J., and Chattanooga, Tenn.

Talc is a relatively abundant mineral, and deposits of talc and soapstone occur in most countries. Pyrophyllite deposits are distributed less widely. Commercial production has been confined mostly to the countries having the highest industrial development. The United States produced 26 percent of the world output of talc, soapstone, and pyrophyllite in 1963; Europe, excluding Russia, 21 percent, and Japan, 23 percent. Almost all Japanese production was pyrophyllite. The free world sources of block steatite talc are India and Italy.

In 1963 talc was produced in Alabama, California, Georgia, Maryland, Montana, Nevada, New York, North Carolina, Texas, and Vermont. Soapstone was produced in Arkansas, California, Maryland, Nevada, Texas, Virginia, and Washington. Pyrophyllite was produced in California and North Carolina. Sericite schist, closely resembling pyrophyllite in physical and chemical properties, was produced in Pennsylvania and included with pyrophyllite statistics.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Talc, in its broader definition, is an inclusive term covering all gradations from the pure mineral to impure, massive talcose rocks (soapstone) that may contain as little as 50 percent of the mineral talc.

Talc, the mineral, is a hydrous silicate of magnesium, $3MgO \cdot 4SiO_2 \cdot H_2O$, theoretically containing 63.4 percent SiO_2, 31.9 percent MgO, and 4.7 percent H_2O. These constituents vary within rather wide limits. Steatite was originally an alternative mineralogical name, often restricted to massive talc (*14*). It also was used to refer to any massive talcose rock. In recent years steatite has been used to designate a grade of talc suitable for making electronic insulators. Specifications for steatite talc state

[2] Numbers in parentheses refer to items in the list of references at the end of this chapter.

the allowable maximum impurities, shrinkage, dielectric properties, and fired color (*13*).

Steatite ceramics are dielectric bodies compounded from ground steatite talc and a suitable flux and binder, formed by dry pressing or extrusion and subsequently fired at relatively high temperatures to form strong finished products. Frequently, these steatite ceramics are improperly referred to only as steatite.

Block talc is any massive talc or soapstone from which products can be obtained by machining.

Block steatite talc is block talc that meets specifications for electronic insulators. Block steatite talc has been designated as strategic; thus, the two grades of block talc are referred to as strategic block talc and nonstrategic block talc.

Lava is a term frequently used in the trade to designate block talc or even the finished product made from block talc.

French chalk is a soft, massive variety of talc used for marking cloth.

Soapstone originally was synonymous with steatite. Now it includes all massive gray to bluish or greenish talcose rocks, which, with a few exceptions, feel soapy and can be carved easily with a knife. Virtually all commercial soapstones are highly ferruginous metamorphic rocks composed of 50 to 80 percent of the mineral talc, intimately mixed with varying proportions of chlorite, amphibole, pyroxene, and mica, as well as pyrite, quartz, calcite, or dolomite. Soapstone, therefore, is a rock rather than a mineral, although the term may be used accurately to refer to massive talc, however pure. Soapstone grades imperceptibly into talc.

Pyrophyllite is a hydrous aluminum silicate similar to talc in properties and in most applications. Its formula is $Al_2O_3 \cdot 4SiO_2 \cdot H_2O$, with 66.7 percent SiO_2, 28.3 percent Al_2O_3, and 5.0 percent H_2O.

Agalmatolite and pagodite are terms applied to massive pyrophyllite from China and Korea, used to produce carved ornaments.

Wonderstone is a term applied to a massive block pyrophyllite from the Republic of South Africa.

Grades of talc usually are identified with the end use; for example, Cosmetic grade, Ceramic grade, Pharmaceutical grade, or crayon stock. Some talcs are distinguished by their crystal shape or structure as acicular, fibrous, or massive; by their mineralogical impurities, as tremolitic; or by such terms as hard or soft, white or offcolor. Similar appropriate terms are applied to grades of soapstone or pyrophyllite.

National Stockpile Specifications P–53 Talc (Steatite) Block and P–53a, Talc (Steatite) Lump, cover the physical, chemical, and electronic requirements for grades of talc designated as strategic or critical.

TECHNOLOGY

Geology

Commercial talc deposits are of two classes, those derived from or associated with ultrabasic igneous rocks and those derived from sedimentary magnesium carbonate rocks. Although there is a considerable variation in each class, talc associated with sedimentary carbonate rocks tends to be whiter and purer than that derived from ultrabasic igneous rocks. High-quality steatite talc usually is associated with sedimentary carbonate rocks and occasionally with quartzites and granites.

Talc ordinarily is formed either under conditions of intensive dynamic disturbance, where the magnesian host rock has undergone severe deformation and squeezing with attendant heat and pressure or where the host rock has been subjected to contact metamorphism or hydrothermal alteration as a result of igneous activity.

Commercial talc deposits contain quartz, calcite, dolomite, magnetite, limonite, and many other impurities. In certain instances some impurities are acceptable and do not preclude commercial use of the talc. For example, the St. Lawrence County, N.Y., commercial talc may contain 30 percent or less of mineralogically pure talc. The tremolite, serpentine, and anthophyllite, although mineralogical impurities, are considered to be part of the talc, but other mineralogical impurities, such as hematite, limonite, and pyrite, are deleterious.

Pyrophyllite occurs in irregular, lenticular, or bedded deposits, usually in areas of intense metamorphism. According to Spence (*19*), it is believed to have been formed by hydrothermal alteration of acidic rocks (andesites, rhyolite, tuffs, slates, schists, etc.). Stuckey (*20*) states that the North Carolina deposits were formed through replacement of acid tuffs and breccias. Minerals associated with pyrophyllite are quartz, sericite, pyrite, chloritoid, chlorite, epidote, zircon, titanite, rutile, zeolites, apatite, certain feldspars, and iron oxides. The North Carolina deposits range from a few feet to 500 feet in width, up to 1,500 feet in length, and more than 500 feet in depth.

Mining

More than 60 percent of the domestic talc, soapstone, and pyrophyllite production is ob-

tained by underground methods. Underground entry may be by adit, inclined shaft, or vertical shaft. When underground openings are entirely in ore and support is necessary, extra care must be taken in placing timbers because of the slippery nature of talc. Some deposits are mined by open-stope and pillar methods, with rock bolting used where necessary; recovery ranges from less than 50 to as much as 65 percent.

Mechanization of underground mines is not extensive, although in recent years diesel-operated mining and transportation equipment has been used in one of the larger California mines, which has a vein of talc approximately 15 feet thick with a 13° dip.

When the talc is to be used in block form or for cutting into crayons, explosives are used sparingly to minimize shattering, and blocks as large as practicable are broken out with bars.

At the quarry of Alberene Stone Division, the Georgia Marble Co. at Schuyler, Va., which closed in 1962, cuts averaging 4 feet in width were made along two benches, each about 7 feet high. About 75 percent of the soapstone removed was waste, partly because of hard spots that made sawing difficult, but chiefly because of small cracks that might cause the slabs to break.

Frequently, different grades of talc are mined selectively or hand sorted. One company in Gouverneur, N.Y., mines several grades of talc by selected loading from various stopes or development openings.

Milling

Talc, soapstone, and pyrophyllite have no end uses in the crude form and usually receive some treatment before being sold, although a few consumers prefer to buy crude talc and prepare it to their own specifications. A small quantity (less than 0.25 percent of the total sales) is sawed into rectangular prisms for marking crayons.

A Vermont firm recovers a flotation product from a mixture of talc, high-iron magnesite, and other impurities. Although talc is one of the most flotable minerals, the occurrence of deposits of talc with satisfactory properties for almost all industrial applications has discouraged widespread interest in beneficiation. The cleanest talc is obtained with pine oil and alcohol frothers alone, but the additional use of such reagents as petroleum sulfonate or short-chain amines is usually required to effect satisfactory recovery (*2*, *8*, *11*). Ore from some deposits is dry screened or washed in trommel screens to remove fines and is then passed over belt conveyers to facilitate the elimination of the larger pieces of waste or low-grade material by handpicking.

Primary crushing in jaw or gyratory crushers is followed by secondary crushing in rotary or disc crushers or in rolls. Hammer mills, with or without air separation, are used for further reduction of particle size to the 40- to 100-mesh range.

Roller mills, in closed circuit with air separators, are the most satisfactory for finer grinding (100- to 325-mesh) of soft talcs or pyrophyllites. Roller mills are sometimes equipped with combustion chambers, permitting simultaneous drying and grinding, or with magnetic separators, or with both.

For more abrasive materials, such as New York talc and North Carolina ceramic-grade pyrophyllite, this stage of the grinding is effected in quartzite- or silex-lined pebble mills, with quartzite pebbles as a grinding medium. These mills are ordinarily in closed circuit with air separators but sometimes are used as batch grinders, especially if reduction to finer particle sizes is required.

Fluid-energy grinding mills, popularly called micronizers, are used to make products of finer particle size than are attainable with standard mills. In a micronizer, the granules of feed drop through a central opening into a steel chamber and are there subjected to an intense mutual bombardment by the impulse of high-pressure air or steam introduced through nozzles around the chamber periphery. Standard particle sizes from 20 microns to less than 1 micron are attained; the product is known as micronized talc.

Talc marking crayons are cut from selected, medium-hard, massive talc or soapstone by circular saws similar to those used in woodworking. The lumps of crude talc are squared with large saws, 18 to 24 inches in diameter, and the resulting blocks are sawed into slabs equal in thickness to the desired width of the crayons. Saws, 6 to 12 inches in diameter, are used to cut the slabs into finished crayons, which are then sorted and packed for shipment. For greatest strength, the crayons are cut lengthwise of the grain of the talc.

USES

Properties that make talc, soapstone, and pyrophyllite desirable for a wide variety of industrial uses include the following: Extreme softness (No. 1 on Mohs' scale), whiteness, good hiding power, good luster, good retention for filler purposes, chemical inertness, high slip, high fusion point, high dielectric strength, high specific heat, varying degrees of oil absorption, low moisture, and low electrical and heat con-

ductivity. Talc is used for marking crayons because it makes a mark on either hot or cold metal that remains visible when the metal is cooled or reheated. All of these properties are not necessarily found to the same favorable degree in an ore from a specific deposit. The ceramics, paint, rubber, insecticides, roofing, and paper industries consumed 79 percent of the talc, soapstone, and pyrophyllite sold or used by producers in the United States in 1963.

Table 1 shows the percentage distribution by uses of talc, soapstone, and pyrophyllite sold by producers in 1959–63 and illustrates the differences in the use patterns of the materials.

Because most talc, soapstone, and pyrophyllite is marketed within a few hundred miles of the source, the use pattern for material from an individual deposit is usually confined to the needs of local industry rather than to the wide range of uses for which it is suitable. Customers, however, frequently insist on certain materials regardless of transportation costs. Table 2 shows the differences in use patterns of ores of each commodity from selected States.

Talc has diverse minor and special uses such as in white-shoe polishes and white-glove cleaners; as a dusting powder for salami; to prevent sticking of bottle, rubber, and candy molds; to impart a finish to wire nails and leather; as a filler in plastics; as an admixture for certain concretes; as a polishing medium for peanuts, gunpowder grains, and turned wooden articles, and as a component of some cup greases.

Nonstrategic block talc is used for gas-burner tips, insulators for electrical appliances, and marking crayons. Strategic-grade block talc is used for tube spacers and insulators for vaccuum power tubes.

Block pyrophyllite is used as a pressure transfer medium in ultra-high-pressure devices and for welding-torch tips, airplane instrument-panel bushings, and components of warheads for guided missiles, among other applications.

TABLE 1.—*Talc, soapstone, and pyrophyllite consumption patterns in the United States, 1959–63 (average)*

[Percent]

Use	Talc	Soapstone	Pyrophyllite
Ceramics	38	3	27
Paints	21	2	1
Rubber	5	4	5
Insecticides	4	36	24
Paper	4		
Roofing	7	23	(1)
Toilet preparations	2		(1)
Textiles	2		
Asphalt filler	2	20	11
Foundry facings	(1)	4	
Refractories	(1)		18
Rice polishing	(1)	(1)	
Crayons	(1)	(1)	
Other	15	8	14
Total	100	100	100

[1] Less than 1 percent.

TABLE 2.—*Talc, soapstone, and pyrophyllite sold or used by producers in the United States, 1959–63 (average), in selected States, by commodities and uses*

[Percent]

Use	Talc					Soapstone				Pyrophyllite	
	California	New York	North Carolina	Texas	Vermont	Arkansas	California	Maryland	Virginia	California	North Carolina
Ceramics	60	46	(1)	70	(1)		11			6	36
Paints	21	34		(1)	6		3			5	1
Rubber	3	1		1	18	1	6	2	15	(1)	8
Insecticides	2	(1)		6	7	71	50		19	58	23
Paper	2	1			15						
Roofing		1		1	31	26		37	35	(1)	(1)
Toilet preparations	2		33		(1)					(1)	
Textiles	(1)	(1)	50		1						(1)
Asphalt filler	(1)			(1)	1	2	11	57			
Foundry facings		(1)			(1)		(1)	3	24		25
Refractories	(1)						(1)				
Rice polishing	2						(1)				
Crayons			4		(1)						
Other	8	17	13	22	21		19	1	7	31	7
Total	100	100	100	100	100	100	100	100	100	100	100

[1] Less than 1 percent.

ALTERNATE MATERIALS

Talc, soapstone, and pyrophyllite are subject to competition from each other, from kaolin, fuller's earth, limestone, and other nonmetallic fillers, and from feldspar for ceramics as determined partly by price and partly by performance. For example, although pyrophyllite is more suitable as a neutral diluent for organic insecticides, talc, soapstone, fuller's earth, kaolin, diatomite, or other substances may be used in areas where pyrophyllite costs much more or when other properties of the filler are more important. Another example is the substitution of kaolin for New York and Vermont talcs as paper filler.

Phosphate-bonded talc is used in place of block steatite talc; potential substitutes are magnesium oxychloride-bonded talc, phosphate-bonded synthetic mica, and hot-pressed syntheic mica.

RESERVES

Quantitative data on domestic talc and soapstone resources are not complete, but about 90 million tons of reserves has been estimated on the basis of available information (*9*). Additional large deposits will probably be discovered in some of the major producing areas for which reserve data are now lacking. The largest known ore bodies, containing over 50 percent of the known reserve, are in New York. The Vermont deposits comprise 30 percent of the reserve, and the remaining 20 percent is distributed between California, Georgia, Montana, Nevada, North Carolina, and Texas.

Essentially all of the domestic talc is of nonstrategic varieties, but deposits in Montana and Nevada contain a few thousand tons of lump steatite similar to the lump material from India. Large quantities of nonlump high-quality talc suitable for electronic applications are also known to exist in those States.

Pyrophyllite reserves in North Carolina total at least 12 million tons (*21*). The pyrophyllite belt is about 75 miles long, extending in a Northeast-Southwest line from Granville County to Montgomery County (*10*). Pyrophyllite deposits in California are located in Mono, Inyo, San Bernardino, and San Diego Counties. Reserve data are not available.

Talc and soapstone deposits are widespread throughout the world with the notable exception of Japan, where there is very little talc. Japan has, however, large deposits of pyrophyllite, a suitable substitute for most applications. The reserve is more than 70 million tons. Only two countries, India and Italy, have significant reserves of strategic-quality lump or block steatite, and only the Indian material is suitable for ultra-high-frequency electronic applications. In India, one of the two adjoining mines was essentially exhausted several years ago; reserves of the other deposit are not known. The Italian strategic block talc is found in Sardina; reserves are large, but quantitative data are not available. Large deposits of nonstrategic talc and soapstone are being exploited in France, Austria, Norway, India, U.S.S.R., and other countries.

SOURCES OF STATISTICAL INFORMATION

Annual data on the quantity and value of production and on sales of crude, sawed, manufactured, and ground talc, soapstone, and pyrophyllite are obtained from a canvass of all domestic producers and are published by the Bureau of Mines. In addition, data on the estimated end use of these materials are obtained from domestic producers in lieu of canvassing the large number of ultimate consumers. No data are published on stocks.

Figures on the quantity and value of imports of crude talc and soapstone and exports of talc, soapstone, and pyrophyllite are compiled by the Bureau of Mines from data obtained by the U.S. Department of Commerce. World production and exports data are compiled from State Department dispatches and official publications of foreign countries.

PRODUCTION, CONSUMPTION, AND TRADE

Table 3 shows world production of crude talc, soapstone, and pyrophyllite, by countries, 1954–58 (average) and 1959–63. Table 4 shows the apparent consumption of these materials in the United States for the same period. From 1930 to 1963, consumption of talc, soapstone, and pyrophyllite increased at a rate about 1½ times that of the gross national product in constant dollars, and no slackening of the rate of increase is apparent. The domestic per capita consumption of these commodities increased from 2.9 pounds a year in 1930 to 8.1 pounds a year in 1958 and remained at about that average level

TABLE 3.—*World production of talc, soapstone, and pyrophyllite, by countries*

[Thousand short tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963
Argentina	31	30	25	25	21	21
Australia	16	19	18	17	17	14
Austria	76	56	91	94	84	72
Brazil	27	23	22	26	42	42
Canada	31	39	42	48	46	55
China	(1)	165	165	165	165	165
Egypt	6	7	7	7	7	5
Finland	8	8	11	7	7	6
France	145	194	207	245	231	214
Germany, West	36	30	32	33	30	30
India	50	71	103	102	114	130
Italy	108	120	137	146	140	149
Japan	338	535	653	700	650	720
Korea, North	(1)	2	4	17	22	22
Korea, Republic of	16	19	25	50	51	71
Norway	95	124	114	120	142	142
South Africa, Republic of	3	1	2	3	14	8
Spain	29	31	31	30	31	30
Sweden	14	16	17	17	18	18
Taiwan	6	7	12	14	15	16
United Kingdom	5	6	7	8	8	8
United States	697	792	734	762	772	804
U.S.S.R.	(1)	275	300	330	340	385
Other countries [2]	11	10	11	34	35	23
Total	[1] 2,020	2,580	2,770	2,990	2,990	3,150

[1] Data not available; estimate included in total except for North Korea.
[2] Includes Colombia (1960–63); Kenya (1954); Greece, Mexico, Paraguay, Peru, Portugal, Swaziland, Uruguay (1954–63); Yugoslavia (1954–58).

in the 1959–63 period. Italy, Canada, and France provided 95 percent of the United States imports from 1949 to 1953, inclusive, and 97 percent from 1954 to 1963, inclusive. Exports from the United States began to rise markedly in 1955 as a result of increased shipments of ceramic-grade talc from Texas to Mexico and amounted in 1963 to nearly 2½ times the 1954 volume.

Tariff rates effective August 31, 1963, on talc and soapstone were: Crude and not ground, 0.05¢ per pound; ground, washed, powdered, or pulverized, 12 percent ad valorem; cut or sawed, or in blanks, crayons, cubes, disks, or other forms, 0.5¢ per pound; other not specifically provided for, 24 percent ad valorem.

TABLE 4.—*Apparent consumption of talc, soapstone, and pyrophyllite in the United States*

[Thousand short tons]

Year	U.S. total sales	Imports for consumption				Exports	Apparent consumption
		Italy	Canada	France	Other countries		
1954–58 (average)	688	17	3	3	1	40	672
1959	782	18	2	4	1	59	748
1960	722	18	2	3	1	60	686
1961	727	20	2	5		48	706
1962	777	19	2	4	1	47	756
1963	794	18	2	5	1	57	763

STRATEGIC CONSIDERATIONS

Block steatite talc is on the list of strategic and critical minerals for stockpiling. The free world supply is concentrated in one deposit in Italy and two adjoining deposits, one now practically depleted, in Madras Province, India. The supply of Italian material exceeds the demand, but Italian block steatite talc is not suitable for ultra-high frequency applications such as power-tube insulators. Indian material can be used for all applications, but production is erratic. The stringency of the block-steatite supply situation has been virtually eliminated by stockpiling and by development of phosphate-bonded talc, which is made from ground steatite talc and phosphoric acid, both in ample domestic supply. Evaluation tests made under contract with the U.S. Army Signal Corps Supply Agency showed that the phosphate-bonded material, although somewhat more difficult to fabricate into tube insulators, is equal in performance to the Indian natural block steatite talc normally employed. The block-talc processing facilities in the United States are concentrated in two plants, one in New Jersey and one in Tennessee. In an emergency the processing facilities could be dispersed readily, because only standard woodworking equipment, such as lathes and drill presses, is required.

Talc, soapstone, and pyrophyllite mines and grinding plants are distributed throughout the United States so that there are no strategic problems in production, but shortages of transportation for such bulk commodities could develop in an emergency.

The United States is self-sufficient in all grades of talc, soapstone, and pyrophyllite except block steatite talc and block pyrophyllite. Annual requirements of these materials are about 2,000 tons. Ceramic-grade pyrophyllite, produced only in North Carolina, is in short supply, but no other world sources of comparable material are known.

GOVERNMENT PROGRAMS

The Office of Minerals Exploration, U.S. Department of the Interior, will advance 50 percent of approved costs on exploration programs for block steatite talc.

PRICES

Prices are negotiated between buyers and sellers on the basis of a wide range of specifications. Quotations only indicate the range of prices. For example, crude soapstone is delivered in Los Angeles for about $5 a ton, California talcs are valued in the general range of $8 to $15 a ton, f.o.b. mines, and ground and bagged material is priced about as follows: Soapstone and grades of talc used mostly as fillers, $17 to $20 a ton; ceramic and paint talcs, $30 to $32; steatite-grade talc, $35 to $40; cosmetic and pharmaceutical talcs, $35 to $50; and micronized talcs, $50 to $100 (*23*). Although a greater variety of grades is produced in California than in most States, the same general price range prevails in other producing areas.

Talc prices quoted in E&MJ Metals and Minerals Markets for December 30, 1963, were as follows: Per short ton, carlots, f.o.b. works, including containers unless otherwise specified: Georgia, 98 percent through 200-mesh, gray, $10.50 to $11.00 and white, $12.50 to $15.00; New Jersey, mineral pulp, ground, bags extra, $10.50 to $12.50; Vermont, 100 percent through 200-mesh, extra white, bulk basis, $12.50 and 99.5 percent through 200-mesh, medium white, $11.50 to $12.50; Virginia (soapstone), 200-mesh, $10 to $12, 325-mesh, $12 to $14, and crude, bulk, $5.50.

Quotations in Oil, Paint and Drug Reporter, December 30, 1963, were as follows: Per short ton, carlots, in bags, f.o.b. works: California,

$34.00 to $39.50; New York, fibrous, ground, $28.00, 99.5 percent through 325-mesh, $31.00, 400-mesh (micronized), $38.00, and 625-mesh (micronized), $80.00; Vermont, offcolor, $19.40; Canada, $20.00 to $35.00.

Pyrophyllite prices have not been published since 1954, when they were given as follows: Per short ton, bulk, carlots, f.o.b. mines: Standard grade, 200-mesh, $12.50, 230-mesh, $13.50, 300-mesh, $16.75; No. 3 grade, 200-mesh, $10 to $12, 325-mesh, $12 to $14, and crude, $5.50.

TAXES

No special taxes are imposed on the talc, soapstone, or pyrophyllite industries. Producers of block steatite talc are granted a depletion allowance of 23 percent on domestic production and 15 percent on foreign production. Producers of all other grades of talc and of all grades of soapstone and pyrophyllite are granted a depletion allowance of 15 percent on either domestic or foreign production.

TRANSPORTATION

Many of the grinding mills in the California-Nevada area are 100 or more miles from the mines. Some California and Montana crude talc is shipped to Utah and Nebraska, and Texas crude talc is shipped 300 to 400 miles for grinding. With these exceptions, grinding mills are near the deposits and have access to the major marketing areas. The better grades of ground talc, however, may be shipped from one coast to the other, despite the relatively high transportation costs.

RESEARCH

Most producers of talc, soapstone, and pyrophyllite have laboratory facilities for controlling the quality of their products, and some of the larger companies conduct research to correlate physical properties with end uses and to evolve new applications. Through research, producers develop specifications for various uses.

The National Bureau of Standards, under contract with the Office of Naval Research, carried out research on the synthesis of fluoro talcs, in which hydroxyl groups are replaced by fluoride ions (*22*).

Improved blending results from a new procedure in which ground talc is introduced upward from the base of the storage silo as a fluidized air suspension. Continuous agitation is thus assured as the filling progresses, and subsequent withdrawal of the stored talc through several ports around the bottom of the silo simultaneously delivers a product of superior uniformity (*16*, *17*).

A new application was announced in which ultrafine micronized talc is used to reinforce synthetic rubbers, ethylene propylene copolymers (EPR) and ethylene propylene terpolymers (EPT) (*15*).

The difficulty of obtaining adequate supplies of block steatite talc during World War II stimulated research by the Bureau of Mines and others that resulted in the development of phosphate-bonded talc as a suitable substitute (*7*). Subsequently, the Bureau of Mines developed a process for producing block talc from ground material with magnesium oxychloride as a bonding agent (*12*).

OUTLOOK

Consumption of talc, soapstone, and pyrophyllite has increased in amount by an average of 20 thousand tons annually for the past 20 years, a rate of increase that is expected to continue. The year-to-year consumption pattern is erratic and difficult to predict.

New uses for talc are expected to develop as finer grinds, precise sizing, and quality stabilization become standard for the producing industry. Recent research has indicated the possibility of improving EPR–EPT rubbers by incorporation of micronized talc. This use alone could require several thousand tons annually within a few years.

Recent consolidations by several talc producers may have pointed the way for similar moves by others in the field to obtain the advantages of national sales, advertising, and managerial organizations.

PROBLEMS

Many of the uses for talc and pyrophyllite can be filled either by other natural materials such as clays, feldspar, kyanite-group minerals, mica, quartz, and wollastonite or by manufactured or processed materials. Competition from these materials imposes limits beyond which it is difficult to develop new talc markets or even to maintain or expand those already existing.

The development of standardized specifications for talc has been hindered by the diversity of physical and chemical properties of the talc and pyrophyllite from different parts of the country.

While the larger producers have developed improved processing methods and can turn out high-quality products with little variation from year to year, the small operators do not have the facilities or capital to achieve and maintain such quality and are therefore at a disadvantage in marketing their products.

Little information is available concerning the influence upon the suitability of fillers for various purposes of such properties as particle size, particle shape, and sorption characteristics. Each deposit has its characteristic properties, so that the application of industry-wide specifications is difficult, but better basic data would be helpful to industry in applying them to any particular deposit.

Many underground talc mines are not well laid out, impeding the use of modern equipment in the irregular haulage drifts, shafts, and stopes.

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TANTALUM

By Richard F. Stevens, Jr.[1]

ALTHOUGH discovered in 1802, tantalum did not assume commercial or strategic importance until the 20th century with the development of the nuclear and space-age requirements for material having elevated-temperature strength properties and with the development of tantalum capacitors for the rapidly growing electronic industry. The demand for tantalum is expanding, but the rate of growth may be limited by an uncertain ore supply. New methods of extractive metallurgy have been developed by the Bureau of Mines which simplify the separation of tantalum and columbium. A process originally developed for titanium and zirconium has been successfully used to reduce tantalum and columbium chlorides to metal. The reduced tantalum metal can then be arc-cast into ingots using consumable electrodes. Electron-bombardment melting, which significantly reduces the impurity content of the metal, also is used to produce high-purity tantalum metal ingots.

The presently known tantalum resources are insufficient to supply the demands of an expanding technology. Exploration for and development of domestic tantalum ores and minerals should be conducted so that the United States will not be completely dependent upon imports. The development of less expensive and more efficient separation processes is required to recover tantalum from its low-grade ores. Physical metallurgy research is required to develop high-temperature tantalum-base alloys.

BACKGROUND

Tantalum was not used commercially until 1903 when Siemens-Halske A.G., Germany, began producing tantalum incandescent-light filaments. The following year production of tantalite for export to Germany started in South Dakota. By 1912 tungsten had replaced tantalum in filaments.

In 1922 Fansteel Products Company marketed a battery charger featuring a tantalum rectifier. By 1927 technological advances largely eliminated the use of radio storage batteries, lowering the demand for tantalum rectifiers; but chemical plants began using tantalum equipment. The use of tantalum expanded slowly through the 1930's, and sintered tantalum capacitors were introduced in 1940.

Ore shortages and increased demand for tantalum during World War II and the Korean war resulted in temporary allocation controls. In 1952 a Government-guaranteed purchase program was instituted to encourage increased production of tantalum concentrate. Termination of Government purchases of foreign tantalum concentrate in May 1955 and of domestic tantalite in December 1958 resulted in lower ore prices. Industrial demand for the minerals, however, increased as new firms began producing the metal. This was encouraged primarily by burgeoning demand for capacitors.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Tantalum mining is predominantly a foreign industry. The Congo (Leopoldville), Brazil, Mozambique, Rhodesia and Malawi (formerly Nyasaland), and Portugal were principal sources of tantalum ore in 1963. World output in 1963 totaled 5,330 tons of columbium-tantalum concentrate. Domestic mine output has consisted of intermittent and highly variable production from many low-grade pegmatite deposits in South Dakota, Colorado, New Mexico, Maine, New Hampshire, and North Carolina, with minor production from a few other States. Euxenite, a columbium-uranium-rare earth

[1] Commodity specialist.

mineral concentrate produced in Idaho, contains potentially valuable quantities of tantalum.

Installed annual domestic production capacity is estimated to be more than 300 tons of tantalum and is expanding. This is many times the installed capacity of the rest of the free world nations combined. U.S. capacity for producing ferrotantalum-columbium is estimated to be about 1,000 tons and capable of rapid expansion if necessary.

Tantalum metal, compounds, or alloys were produced during 1963 by the following domestic firms: Fansteel Metallurgical Corp., North Chicago, Ill., and Muskogee, Okla.; Kawecki Chemical Company, Boyertown, Pa.; Kennametal Inc., Latrobe, Pa.; National Research Corp., Newton, Mass.; Union Carbide Metals Co., Niagara Falls, N.Y.; and Wah Chang Corp., Albany, Oreg. Tantalum metal, compounds, or alloys were produced by the following foreign firms: Murex Limited and Blackwell's Metallurgical Works, Ltd., England; Fansteel-Hoboken S.A., Belgium; Herman C. Starck A.G., Gesellschaft für Electrometallurgie, and Heraeus Quarzschmelze, Germany; Metallwerke Plansee, Austria; Kovametalli Oy, Finland; Société des Produits Pharmaceutiques Ciba, Switzerland; and Kobe Steel Works, Ltd., Japan Vacuum Engineering Co., Ltd., Shin-Etsu Chemical Industry Co., Ltd., and Taiyo Metal Industries Co., Ltd., Japan.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Tantalum is characterized by high melting point, resistance to corrosion, and ease of fabrication. At elevated temperatures the metal is an excellent interstitial absorber of common gases. It is a relatively good conductor of heat and electricity and an excellent thermionic emitter of electrons in vacuum tubes. The metal exhibits a rectifying or electronic valve action in an electrolyte. It is twice as dense as steel and has a moderately high thermal-neutron-capture cross section of 21 barns.

Tantalum metal is sold in several grades from 95 to 99.9 percent purity. Tantalum concentrate is nominally sold on the basis of 60 percent contained Ta_2O_5 but substantial lower grade concentrate is used. Stockpile specifications for tantalum minerals require a content of at least 40 percent Ta_2O_5 and that Ta_2O_5 be equal to or in excess of Cb_2O_5.

TECHNOLOGY

Geology

Tantalum is recovered mostly from pegmatite deposits and weathering products of pegmatite or granite. The current production from bedrock is of minerals of the columbite-tantalite series and minor amounts of microlite. The residual and placer production is all columbite-tantalite except in Idaho, where the principal mineral, euxenite, contains some tantalum.

The amount of tantalum in the crust of the earth has been estimated at 0.00021 percent. Characteristic geochemical associations are most often with columbium, rare-earth elements, titanium, zirconium, and tin (*2*).[2]

The principal tantalum minerals are microlite, fergusonite series, stibiotantalite series, tapiolite-mossite series, columbite-tantalite series, euxenite-polycrase series, eschynite-priorite series, betafite series, samarskite, and struverite.

Mining and Concentration

Depending upon labor and power supply and upon the geologic nature of the deposit, mining methods extend from hand labor through giant dredges to highly mechanized open-pit mining operations. Underground mining is restricted to relatively shallow inclines and shafts which have followed rich ore shoots beyond the practical limit of opencut mining techniques. Tantalum concentrates are produced by hand separation or by various combinations of gravity, magnetic, and electrostatic separation.

Metallurgy

Columbium and tantalum are extracted from mineral concentrates by fusion with hot sodium hydroxide followed by leaching with water and then with hydrochloric acid to remove impurities. The insoluble columbium-tantalum residue is dissolved in anhydrous hydrogen fluoride, potassium hydroxide is added, and the batch is cooled to precipitate potassium-tantalum fluoride, leaving the more soluble potassium-columbium oxyfluoride in solution.

Solvent extraction, a process by which a metallic salt is selectively transferred from one to the other of two immiscible liquids, is used by some companies to produce separated tantalum and columbium oxides. A new plant in California separates columbium and tantalum by fractional distillation of their chlorides. Other methods of extractive metallurgy have been developed by the Bureau of Mines to separate tantalum and columbium (*3*, *6–7*). Physical metallurgy research conducted by the Bureau has evaluated tantalum-base alloys for elevated-temperature applications.

Tantalum reduction is usually done by electrolysis of potassium-tantalum fluoride. Tan-

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

talum metal is produced at the cathode as a fine crystalline aggregate which disperses in the molten electrolyte.

A less widely used commercial method of tantalum reduction consists of mixing dried potassium-tantalum fluoride with metallic sodium and heating the mixture in an evacuated vessel. Some metal is produced in Europe by hydrogen reduction of tantalum chloride. Tantalum metal also is prepared by heating a mixture of pentoxide and tantalum carbide in a vacuum.

Tantalum powder or sponge can be converted into massive metal by vacuum sintering, by melting in a consumable or nonconsumable electric arc furnace, or by electron-beam melting.

Fabrication

Tantalum, when hot, readily absorbs gases that cause embrittlement, and all forming, stamping, and drawing is done cold. The metal seizes and tears easily and requires caution during machining operations. Tantalum work-hardens at a much slower rate than most other metals and thickness reduction of 60 percent or more without an intermediate anneal is standard practice. Rolling tantalum to half-mil or quarter-mil foil for capacitor use is accomplished on a precision Sendzimir rolling mill.

Tantalum can be welded to itself and a number of other metals by either resistance welding or inert-gas arc welding.

USES

Ferrotantalum-columbium (approximately 40 percent Cb and 20 percent Ta) is added to certain steels or high-temperature alloys.

An alloy of 92.5 percent tantalum and 7.5 percent tungsten maintains its elasticity at high temperatures and is used to manufacture electronic tube components such as filament and grid coil springs. Other tantalum-tungsten alloys are used in experimental rocket-engine parts.

Tantalum capacitors are characterized by high capacity in a small volume, stability of the oxide film, workability over a wide temperature range, long shelf life, and low reverse current (back leak). The tantalum anode acquires its dielectric property from a thin tenacious oxide film formed by anodic oxidation before assembly. This field is the largest consumer of tantalum metal.

Tantalum rectifiers are used in low-voltage applications such as railway signals, highway crossing devices, and battery charges.

Tantalum is a preferred material for use as a getter and electron emitter in electronic tubes. The metal also offers a high melting point, ease of fabrication, and efficient thermionic electron emission.

A new type of miniature electronic valve, the cryotron, consists of a tiny strip of tantalum around which a fine columbium wire is wrapped. The combination becomes superconductive at about −270° C. Such a component has a considerably lower power consumption than a thermionic valve, and a hundred such devices will fit into a thimble. They offer revolutionary possibilities for computer design and great improvement in radar devices.

The remarkable inertness of tantalum and its other properties make the metal suitable for equipment used in handling acids. Its corrosion resistance and strength permit thinner gage metal to be used in heat exchangers resulting in higher heat-transfer efficiency. Tantalum crucibles are the best available for melting certain metals.

Tantalum, because of its resistance to attack by body acids and its compatibility with body tissue, is used for sutures, for sheet and plate for cranial repair, to mend broken bones, and in both surgical and dental prosthetics.

Because it is insoluble in plutonium, tantalum was used as the fuel-container material in the Los Alamos Molten Plutonium Reactor Experiment. It is being considered for use as the fuel container in other fast reactors where resistance to corrosive action of the fuel is of extreme importance and the thermal cross section is unimportant. It may also prove useful in reactor heat-exchanger systems.

Tantalum carbide can be used separately or blended with other carbides in forging dies, cutting tools, jet-engine turbine blades, valves, valve seals, valve guides, and rocket nozzle coatings.

Tantalum oxide was used during World War II as a catalyst to produce butadiene from alcohol. The process has since been replaced by a more economical one, which does not require the use of tantalum-bearing catalysts.

Tantalum 182 radioisotope is produced at Oak Ridge National Laboratory for use as a radioactive tracer element. Tantalum is also used in spinnerets for synthetic fiber production, surgical and dental instruments, laboratory ware, anode baskets for electroplating devices, extrusion rings for the manufacture of synthetic sausage casings, special optical glass, and high-voltage surge arresters.

BYPRODUCT AND COPRODUCT RELATIONSHIPS

Columbite-tantalite ores are usually coproducts and in some cases are associated with other valuable minerals such as cassiterite, mica, feldspar, beryl, and spodumene. In more intimate

association, columbium and tantalum may share a crystal lattice with rare-earth metals, tin, uranium, zirconium, titanium, thorium, phosphorus, and calcium. The particular suite of valuable constituents in a given deposit often determines whether or not it can be profitably worked.

Tin smelter slags and tin mine tailings are sources of columbium-tantalum. Although current practice is to separate most of the columbium-tantalum concentrate by magnetic means at the mine while the remainder of the columbite-tantalite reports with the tin concentrate, some tailing piles contain significant quantities of columbium-tantalum minerals.

ALTERNATES AND SECONDARY SOURCES

In electronic uses, alternate rectifier materials include aluminum, silicon, germanium, and selenium. Zirconium, titanium, and misch metal are substitutes as getters in vacuum tubes. Possible replacements for tantalum corrosion-resistant equipment are platinum, columbium, and zirconium.

Data are not collected on utilization of tantalum scrap. A substantial quantity, such as worn tantalum chemical equipment, is reclaimed.

RESERVES AND RESOURCES

Reported free world tantalum resources total less than 100,000 tons of contained Ta_2O_5 (*2*), much of which is economically unrecoverable. Whether there are sufficient ore resources to supply an expanding long-term demand is questionable.

Deposits of tantalum ore, primarily associated with columbium, have been reported in North America, South America, Europe, Africa, and Oceania. Over 80 percent of the economically recoverable tantalum is obtained from Africa and South America, making the United States almost completely dependent upon overseas supplies for tantalum.

The principal foreign sources of tantalum metal are columbite-tantalite and microlite from pegmatites, and residual deposits associated with pegmatites, placers, tin tailings, and smelter slags.

SOURCES OF STATISTICAL INFORMATION

Data on domestic production and consumption of tantalum concentrates and production of the metal, alloys, and compounds are obtained by the Bureau of Mines through industry canvasses. Satistical data on imports and exports of concentrates and products are obtained from the Bureau of the Census. Data on world production of concentrates are compiled by the Bureau of Mines from the information supplied by foreign service dispatches and by official publications of the Departments of Mines of various foreign countries and from other sources.

PRODUCTION, CONSUMPTION, AND TRADE

Since 1940, the United States has been the leading consumer of tantalum ores, but domestic mine production of tantalite has been negligible. Virtually all of the U.S. tantalite supply is imported; 73 percent of 1963 imports were from the Eastern Hemisphere and 27 percent were from South America. Salient tantalum statistics are presented in table 1.

Tantalum ore and concentrates and columbium-tantalum-bearing tin slags are imported duty free. Duties on tantalum-bearing metal scrap have been suspended by Public Law 869 (1950) as amended and extended. Duty on the metal and its alloys is 10 percent, ad valorem, effective August 31, 1963, under the "Tariff Schedules of the United States, Annotated (1963)." For Communist nations, the statutory rate of duty of 25 percent, ad valorem, remains in force.

STRATEGIC CONSIDERATIONS

The domestic tantalum industry is almost entirely dependent upon imports for its ore supply. Because of the dependence upon Eastern Hemisphere and South American supplies, it was necessary during the peak of World War II submarine attacks to airlift high-grade ore to the United States for military uses. Dependence will continue on overseas sources of tantalum ores. Tantalum ore reserves are not large and if the demand for such ore should increase drastically, the search for new ore supplies would have to be greatly accelerated.

Although a new tantalum stockpile objective of 3.4 million pounds was announced on March 20, 1964, the quantities of tantalum concentrates, compounds, and alloys stockpiled by the Government are considered to be satisfactory for all potential emergency requirements. Foreign acquisitions, except through barter, have been terminated, and no further domestic contracts are planned. On June 30, 1964, Government stocks totaled 3.1 million pounds, of which 1.6 million pounds was in the national (strategic) stockpile, 1.5 million pounds in Defense Production Act stocks, and 35 pounds in the supplemental stockpile.

TABLE 1.—*Tantalum salient statistics*

[Pounds]

	1954–58 (average)	1959	1960	1961	1962	1963
United States:						
Imports:						
Tantalum mineral concentrate	1,213,255	652,839	709,936	1,004,151	1,211,757	944,459
Tantalum metal, compounds, and alloys	[1] 3,029	[2] 1,565	[2] 5,123			2,025
Exports:						
Tantalum mineral concentrate	[3] 4,263	10,337	32,406		36,322	56,010
Tantalum metal, compounds, and alloys [4]	[1] 5,866	6,495	21,469	28,930	34,761	58,666
Tantalum metal powder	[3] 5,950	1,988	1,174	5,585	7,445	14,146
Industrial consumption:						
Contained metal [5]	424,800	466,000	578,000	828,000	946,000	502,000
Ferrotantalum-columbium	[1] 252,800	116,000	130,000	74,000	104,000	34,000
Industrial production:						
Metal	[6] 200,000	244,000	300,000	484,000	514,000	418,000
Ferrocolumbium and ferrotantalum-columbium [7]	[8] 558,000	709,947	847,968	1,156,051	1,573,915	1,575,943
World: Production of columbium-tantalum concentrate [9]	7,990,000	6,040,000	7,020,000	7,540,000	9,210,000	10,660,000

[1] Average of 1955–58 only.
[2] Columbium and tantalum metals and alloys. Separate statistics for tantalum are not available.
[3] Average of 1956–58 only.
[4] Columbium and tantalum metals and alloys in crude and semifabricated forms, and scrap. Separate statistics for tantalum are not available.
[5] Tantalum content of all raw materials consumed, includes columbite, tantalite, and tin slag.
[6] Data for 1958 only; data for previous years unavailable.
[7] Individual production statistics for ferrotantalum-columbium are not available.
[8] Average of 1957–58 only.
[9] Separate statistics for tantalum ore are not available. Does not include tin slags.

The Office of Minerals Exploration encourages exploration for tantalum ores in the United States and its territories and possessions by advancing 50 percent of approved costs of exploration.

PRICES

Although tantalite prices were quoted in the trade papers during 1963 at $6 to $7 per pound of 60 percent tantalite, actual sales were a matter of negotiation in the market. They were primarily determined by the variation in tantalum-columbium ratio and the total tantalum oxide content.

Tantalum was quoted (per pound) at $30 to $49 for powder, $47 to $60 for sheet, and $52 to $65 for rod.

TAXES

Depletion allowance for domestic producers of tantalum ore is 23 percent, and for U.S. producers with production in foreign countries, 15 percent.

TRANSPORTATION AND STORAGE

Transportation and storage of tantalum ores or concentrates present no special problems. For stockpiling, they are packed in 55-gallon galvanized steel drums, but commercially shipments are made in cotton or burlap bags, wooden kegs, or steel drums.

Tantalum powder and pellets are usually packed in sealed polyethylene bags in steel drums. The fluoride of the metal is soluble in water and will hydrolyze to hydrofluoric acid. The containers must be kept dry at all times to prevent production of the highly corrosive acid fumes. Satisfactory containers for the fluoride include rubber-lined drums or coated fiber containers.

RESEARCH

Research on tantalum has greatly accelerated in the past 15 years. The Bureau of Mines has been evaluating resources and studying extraction, separation, and reduction of the metal, including sampling and evaluation of potential domestic resources, beneficiation studies of columbium-tantalum-bearing minerals in alluvial deposits in the Northwest, extraction of columbium and tantalum from low-grade ores and tin slags, separation by solvent extraction, anhydrous separation, reduction techniques, analytical techniques, and preparation of high-purity metal and alloys (*1*, *3*, *6–7*, *10*). Other government agencies engaged in or sponsoring tantalum research include the Atomic Energy Commission on nuclear applications, the Defense Department and National Aeronautics and Space Administration on high-temperature and electronic uses, and the Geological Survey on mineral deposits. Research sponsored by the U.S. Air Force has been primarily concerned with the development of oxidation-resistant coatings for tantalum (*4*, *11*, *12*). Industry and institutions have numerous research programs underway, including research on high-purity metal production, improved high-temperature alloys, and other problems.

OUTLOOK

Tantalum consumption in electronic and high-temperature applications is increasing. Tantalum and tantalum-base alloys will find increasing use as high-temperature cladding and structural material in fast nuclear reactors. Since it is insoluble in plutonium, tantalum is one of the few metals which can be used to clad this extremely reactive metal.

Unless additional sources of supply of tantalum are discovered the presently known deposits of tantalum ore will be insufficient to meet the growing demands of the nuclear and space age.

PROBLEMS

The primary problem associated with tantalum is that of supply. Although the supply of tantalum is adequate for the immediate future, the long-term supply required to meet the projected high-temperature demands of the nuclear and space industries will be inadequate under the present conditions of extractive technology.

The lack of data on domestic and world ore reserves, the dependence of the domestic metals industry upon water-borne imports of tantalum ores, and the lack of extractive methods to recover tantalum economically from low-grade domestic ores will prevent the wider use of tantalum owing to the inability to assure material for future requirements.

Present processes of extraction, separation, reduction, and purification of tantalum metal and of analytical techniques are expensive and hampered by incomplete basic metallurgical and chemical data on tantalum metal, alloys, and compounds.

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TELLURIUM

By Arnold M. Lansche [1]

ONE of the rarest elements, tellurium has never been found in large quantities, nor is its distribution widespread. Its occurrence is comparable to that of gold, with which it is frequently associated. In chemical and physical properties, the element is similar to selenium and sulfur; in its common form, it resembles antimony.

Domestic production of tellurium in 1963 was 201,000 pounds valued at about $1 million. This quantity was 64 percent of world output. It was obtained as a byproduct of base metal refining. The United States is the major producer in the free world.

Thermoelectric devices, metallurgy, and the chemical, rubber, and ceramic industries use tellurium. Great interest is centered on the use of metallic tellurides to convert heat to electricity and to utilize electricity for cooling or heating. There is increasing usage of tellurium in the preparation of the important free-machining steels.

The most important tellurium problem is the need for definitive knowledge of the tellurium resource base. Tellurium needs uses that will annually require constant significant quantities.

BACKGROUND

Tellurium was discovered in 1782 by J. F. Müller von Reichenstein while examining auriferous ores from Siebenbürgen, Transylvania. It had been believed by early chemists that this ore contained an alloy of bismuth and antimony. When he found no trace of either, von Reichenstein published his conviction that the ore contained a new element. His work was later confirmed independently by Bergmann and Kitaibel. In 1792 Klaproth demonstrated conclusively that the new element existed when he extracted it and determined some of its properties. Tellurium was named after the Latin word "tellus," meaning earth, the genitive of which is "telluris."

Commercial production of tellurium began in the United States in 1918. Output was not reported, however, until 1926 when 917 pounds valued at about $1,850 was produced. In 1963 production was 201,000 pounds.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

The world's tellurium industry is organized mainly around the electrolytic copper refineries as a byproduct material. Companies reporting tellurium production in 1963 were American Metal Climax, Inc., Carteret, N.J.; American Smelting and Refining Company, Baltimore, Md.; International Smelting & Refining Co., Perth Amboy, N.J.; Penn Rare Metals, Inc., Revere, Pa.; Phelps Dodge Refining Corp., New York, N.Y.; and United States Smelting, Refining, and Mining Co., East Chicago, Ind. In January 1964 it was announced that Kawecki Chemical Co., Boyertown, Pa., bought Penn Rare Metals, Inc.

The geographic distribution of the free-world tellurium industry closely follows the pattern of the world's electrolytic copper and lead (*1*)[2] refineries, as well as of the fire refining of lead. The United States produced 64 percent of the tellurium output of 1963. Canada, Japan, and Peru accounted for the remainder. The U.S.S.R. is believed to have produced significant quantities of tellurium as a byproduct from sulfide-ore processing.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Tellurium is normally marketed as a steel-gray, minus 200-mesh powder. The pulverized

[1] Commodity specialist.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

tellurium is packed in cartons and cans. The powder is 99.5+ percent pure. Tellurium of similar quality is also marketed in slabs, tablets, and sticks.

A typical analysis of commercial-grade tellurium is 99.7 percent tellurium, 0.003 percent lead, 0.02 percent selenium, 0.004 percent silica, and 0.015 percent copper.

High-purity tellurium, 99.999+ percent, is marketed in 1- and 2-pound plastic containers as crystals usually less than 1 inch long. Cakes about 5 pounds in weight are also available in sealed plastic bags. Maximum level of impurities, copper and iron, is less than 1 part per million. Total halogens, sulfur, and selenium do not exceed 5 parts per million. Silicon, lead, or magnesium also may be present as minute impurities.

Other tellurium materials include 99.99+ percent metal, a powder containing 94 to 95 percent tellurium dioxide, ferrotellurium containing 50 to 58 percent tellurium, and a tellurium-copper alloy containing 40 to 50 percent tellurium.

Tellurium and its compounds have a toxicity similar to but less than that of selenium. When very small quantities of volatile tellurium are absorbed by the human body it imparts a strong garlic odor. This characteristic odor leaves no permanent ill effects and is caused by the formation of organic methyl telluride in the human system. Several drugs, including ascorbic acid and chlorophyll, prove very effective in combating this offensiveness, but the treatment is a prolonged one generally requiring many months. The hazard is controlled by removing tellurium fumes by mechanical ventilation or hooding and the use of respirators.

Thermoelectricity is electricity produced by direct conversion of heat to electricity, but the term is used broadly to denote the interconversion of heat and electricity. The conversion of heat to electricity, known as the Seebeck effect, was discovered in 1822. The inverse, or Peltier effect, whereby electricity can be converted to heat or cold, was discovered in 1834. Tellurium and certain of its compounds have the highest thermoelectric performance characteristics over the medium temperature range.

Seebeck effect.—Seebeck discovered that a voltage was developed in a loop containing two dissimilar metals, providing the two junctions were maintained at different temperatures. This is the basic principle of thermocouples, which have been used for many years. Now the principle is being considered for the production of electric power.

Peltier effect.—Peltier discovered that the junction between two dissimilar metals acted as a heat sink or as a heat source, depending on the direction of the electric current. This is the basis of thermoelectric refrigeration.

TECHNOLOGY

One of the least abundant elements, tellurium is about 1×10^{-6} to 1×10^{-9} percent of the earth's crust. Tellurium minerals may be formed in almost any stage of the ore-forming processes. Its occurrence is similar to that of gold, with which it is often associated, although it is seldom found in the native form. More than 40 distinct tellurium minerals are known, but at present none of these is exploited for tellurium alone.

The major tellurium minerals follow:

Name	Composition	Percent tellurium
Tellurium, native	Te	92–100
Calaverite	$AuTe_2$	56–58
Petzite	$(Ag, Au)_2Te$	32–35
Sylvanite	$(Ag, Au)\ Te_2$	60–63
Hessite	Ag_2Te	35–38
Rickardite	Cu_4Te_3	59–60
Altaite	PbTe	37–39
Tetradymite	$Bi_2(Te,S)_3$	33–49

Of lesser importance are the minerals montbrayite, krennerite, empressite, weissite, emmonsite, nagyagite, coloradoite, joseite, tellurbismuth, and wehrlite.

Tellurium has also been detected in the eruption products of Mount Vesuvius, Italy, in the orange-red sulfur of Japan, and in pyrite from Spain. The most noteworthy occurrences of the element at gold camps are at Cripple Creek, Colo.; Great Boulder Reef, Kalgoorlie, Western Australia; Kirkland Lake, Ontario; and Angel Camp, Calif. High tellurium values have been reported in bismuth deposits of Bolivia. Goldschmidt reported 0.1 gram of tellurium per ton in meteorites, but not any in the sun (*4*).

Tellurium is mined, beneficiated, and smelted along with the coproducts copper and lead. Its presence in gold ores is a serious handicap in recovering the gold because it hinders amalgamation and cyanidation. Such gold ores usually must be concentrated and/or roasted to remove the tellurium as early as practicable from the extraction circuit.

Modifications in tellurium-refining methods are closely guarded trade secrets, and modifications which different companies make in the standard flowsheet are not disclosed. Processing begins with a tellurium-bearing anode slime from the electrolytic refining of copper and lead, which is usually minus 200-mesh. About 8.3 pounds of solids containing recoverable quan-

tities of copper, lead, selenium, tellurium, gold, and silver are obtained from a ton of anode.

The anode slime is leached in acid solution for copper removal and then fused with sodium bisulfate to convert residual copper to copper sulfate and volatilize part of the selenium. The fused cake is granulated and leached with water to remove the copper sulfate. A subsequent leach with caustic soda solution extracts the tellurium. Residue from the double leach is refined in a doré furnace for recovery of precious metals. The tellurium is recovered from the caustic solution by acidulation to precipitate a tellurium oxide sludge that is subsequently refined to metal.

USES

Tellurium and tellurium compounds are used in thermoelectric devices and metallurgy, and by the chemical, rubber, and ceramic industries.

There is increasing interest in combining tellurium with other materials to make use of the phenomenon of thermoelectricity. Lead telluride, bismuth telluride, cadmium telluride, bismuth - tellurium - selenium - antimony alloy, silver telluride, and germanium telluride are some of the alloys successfully used in thermoelectric devices. These alloys perform excellently in converting heat into electricity and in utilizing electricity to cool or to heat. In these devices, the generation of heat depends on the direction of electron flow rather than on ohmic resistance to electricity, as generally known.

Tellurium is added to nonferrous metals to modify certain physical characteristics. Tellurium increases the ductility of aluminum, imparts extreme hardness with a high maximum stress to tin, and improves the machinability of copper without seriously impairing conductivity. Tellurium-lead alloys are tougher, stronger, and more resistant to fatigue, corrosion, abrasion, and vibration than ordinary lead and are widely used for linings of tanks, for heating coils, and for other special equipment for the chemical industry. Lead-base tellurium alloys are widely used in Europe for cable covering and sheathing. Tellurium also increases the corrosion resistance of some magnesium-base manganese alloys.

Addition of a small quantity of tellurium to chilled cast iron acts as a powerful carbide stabilizer and markedly increases the depth of chill. This chilled cast iron is preferred for applications such as railway car wheels, gears, and camshafts. Added to special steels, in quantities reported to range from 0.023 to 0.057 percent, tellurium acts as a degasifier and also improves machinability. It reduces the annealing time of large malleable-iron castings. Other metallurgical uses of tellurium include staining silver. Tellurium-bearing slime is used as a catalyst for removing cobalt in the Tainton process for producing electrolytic zinc.

The uses of tellurium in the chemical industry are comparable to the uses of sulfur and selenium, but both of these elements are superior to tellurium for most chemical uses, and few significant applications have materialized. Consequently, the chemical uses of tellurium and its compounds are often only temporary outlets involving relatively small quantities. One use for tellurium and its compounds is in the field of chemical coloring as a component in the manufacture of the highly competitive organic and inorganic dyestuffs. Tellurium is used for making ultramarine, black, blue, red, and brown colorants used in coloring glass, ceramics, and lithopone. Tellurium is also a chemical catalyst.

Tellurium and its compounds are secondary vulcanizing agents in the processing of both natural and GR–S synthetic rubber. Tellurium diethyldithiocarbamate is the fastest accelerator for butyl rubber manufacture. The normal percentage of tellurium added is generally less than 0.5 percent. The tellurium additives increase the vulcanizing rate, improve aging and mechanical properties, eliminate porosity, and increase the resistance to heat and abrasion. Specific applications include its use in rubber-jacketed cables in the mining, dredging, and welding industries and for conveyor belts.

Colloidal tellurium is an insecticide, germicide, and fungicide. Soluble tellurium compounds are used in photography in toning baths. Tellurium vapor will emit light similar to sunlight under appropriate excitation.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Anode slime produced during electrolytic refining of copper is the chief source of tellurium. Coproduct materials include gold, lead, selenium, and silver. Tellurium and selenium are separated from each other after the other elements have been removed. It is uneconomical to recover tellurium from anode slime without recovering the precious metals also.

ALTERNATE MATERIALS

Selenium often is used in place of tellurium in metallurgy, ceramics, rubber materials, and thermoelectric devices.

SECONDARY SOURCES AND RECOVERY

Production of tellurium from secondary sources is negligible. The use of the element in old scrap-source products, such as thermocouples, will not generate secondary source materials in significant quantities for several years.

RESERVES

The estimated domestic indicated and measured copper reserve is 32.5 million tons of refined copper. The quantity of recoverable tellurium, theoretically contained in the domestic copper reserve based on the rate of 0.20 pound of tellurium per ton of copper, is 6.5 million pounds. The quantity of tellurium recoverable from lead reserves raises the total to 7.2 million pounds of tellurium. Estimates of tellurium resources outside the United States are not available. There is an unmeasured potential resource of tellurium in gold-silver ores, base metal ores, and minor metal tellurides.

CONSERVATION PRACTICES

The value, rarity, and useful properties of tellurium stimulate efforts to recover it from source materials rather than discard it as waste.

SOURCES OF STATISTICAL INFORMATION

Statistics on production, shipments, and stocks are received quarterly and annually by the Bureau of Mines from producers of tellurium and tellurium compounds. These data are on company confidential basis, and the data of the individual companies are combined to provide the published totals. Six companies supplied data in 1963. Records of imports of tellurium are available from the Bureau of the Census, U.S. Department of Commerce.

Statistical coverage for the United States is relatively complete.

PRODUCTION, CONSUMPTION, AND TRADE

In 1963 domestic output of tellurium was 201,000 pounds, valued at about $1 million, general imports 2,000 pounds, producers' stocks 141,000 pounds, and shipments to consumers 134,000 pounds. In 1959 total supply (production, stocks, and imports) almost balanced the large tellurium demand as expressed by shipments to consumers. Total supply in 1959 was 251,000 pounds compared with 257,000 pounds of shipments. That was the first time since 1939 that tellurium supply and demand have so nearly balanced.

Annual free world production was reported in Canada, Japan, Peru, and the United States in 1959–63. The rank, in descending order, was the United States, Peru, Canada, and Japan. Free world output in 1963 was 315,800 pounds of which about 75,000 pounds was produced in Canada, 26,600 pounds in Peru, and 13,300 pounds in Japan.

Imports in 1959–63 totaled 38,250 pounds and came from Australia, Canada, Japan, Peru, Switzerland, the United Kingdom, and West Germany. Imports were sporadic; in 1961 and 1962 there were none. Canada and Peru exported to the United States during 2 years of the period while each of the other countries sent tellurium during only 1 year.

The tariff was adjusted on August 31, 1963, the metal at 8 percent and the compounds at 10 percent. The statutory rate is 25 percent for both metal and compounds.

STRATEGIC CONSIDERATIONS

The United States is self-sufficient in tellurium, and Canada has an adequate supply. Neither the metal nor its compounds are included in the "National Stockpile List of Critical and Strategic Materials." Most producers are in the highly industrialized eastern part of the United States; in Maryland, New Jersey, New York, and Pennsylvania. One producer is at East Chicago, Ind.

GOVERNMENT PROGRAMS

The Office of Minerals Exploration includes tellurium among minerals and mineral products eligible for government financial participation up to 50 percent of approved costs.

PRICES

The price of commercial-grade powder tellurium increased sharply in the period 1959–62 from $1.65 to $6 per pound, or 264 percent. Throughout 1963 the price was $6 per pound. The high-purity grade, 99.999 percent, was $25 per pound in 1959–60, $21.50 to $30 per pound in 1961–62, and $21 to $30 per pound in 1963.

TAXES

There are no special taxes on tellurium. Producers are granted a depletion allowance of 15 percent on domestic and foreign production.

TRANSPORTATION

There are no shipping regulations for tellurium metal or its compounds. High-purity tellurium is shipped and stored in sealed plastic bags.

RESEARCH

A bibliography with abstracts of current literature on tellurium research is compiled and issued monthly by Battelle Memorial Institute for the Selenium-Tellurium Development Association, Inc. (*5*).

A process for converting waste heat into a valuable asset by means of a lead telluride thermoelectric element has been developed (*3*). Lead telluride, as strip or wire, in contact with another metal forms a thermoelectric element capable of converting heat directly into electricity. This system is far superior to ordinary thermocouples in converting heat to electricity in two ways: (1) much larger currents are developed and (2) conversion efficiencies are more than 20 times higher.

Experimental work has been performed on many metallic tellurides to determine the Seebeck coefficient, the resistivity, and the thermal conductivity (*2*). Some of the more promising materials examined were gold-antimony-bismuth teluride, lithium-manganese telluride, bismuth-selenium telluride, antimony-selenium telluride, silver-germanium-antimony telluride, silver-antimony telluride, bismuth-tellurium sulfide.

OUTLOOK

Some economic uses for tellurium have been developed. Several metallic tellurides, which are desirable for use in thermoelectric devices have been produced. Tellurium is used in produring free-machining steels which have been a welcome addition to the steel-shaping industry. The short-term and long-term outlooks are for an adequate supply and a slowly accelerating consumption. Competitive materials will continuously challenge any uses of tellurium because of its scarcity, high prices, and apparent lack of superior or unique properties. However, in an expanding economy where all kinds of commodities are in demand, it is anticipated that there will be a place for tellurium despite competition.

PROBLEMS

Tellurium problems are directly proportional to the level of demand. The most important problem concerns the need for greater knowledge of the potential resources of tellurium because the element has applications in which large quantities would be consumed if available. The problems related to detection, exploration, and extraction are expected to be routine. Substitution is a perennial problem for tellurium because of price and inelastic supply. Tellurium needs uses that will annually require reasonably constant significant quantities. The odor and toxicity of tellurium are problems with which industry must contend.

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THALLIUM

By Harold J. Schroeder [1]

THALLIUM, a relatively rare element in the earth's crust, was discovered about 100 years ago by Crookes. It is found associated with many minerals, but not in deposits of sufficient size and tenor to be processed for thallium alone, and its sole domestic source is as a byproduct from flue dusts at zinc smelters. It is best known for its odorless, tasteless, and very poisonous sulfate, which is used as a rodenticide. In addition to this use, small quantities are used in electronics and in alloys for bearings, solders, and fusible alloys.

The domestic resource of thallium in zinc sulfide deposits alone is substantial, although at present most of the resource from zinc-smelting operations is wasted because there is little demand for thallium. The United States is self-sufficient in thallium, and it is not stockpiled by the Government.

Present prices of thallium are $7.50 per pound for the metal and $5 per pound for thallium sulfate; 99.999 percent thallium is available at a higher price.

Research on thallium by industry, institutions, and government has been limited. There is a need for research to develop more uses for the element before the outlook for thallium can be considered good.

BACKGROUND

Sir William Crookes, an English scientist, discovered thallium in 1861 while making spectroscopic examinations for tellurium on a residue from a sulfuric acid plant in Germany. Crookes named the new element thallium from the Latin word thallus, meaning budding twig, because its spectrum resembled the color of young vegetation. Shortly thereafter Crookes produced a few grains of the metal. During the following year, A. Lamy, a French scientist, found thallium in a residue from roasting Belgian pyrite for sulfuric acid and recovered several hundred grams of the metal to study its chemical and physical properties.

SIZE AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Thallium metal and compounds are produced in the United States by the American Smelting and Refining Company at its Globe, Colo. refinery.

Countries presently producing thallium are Belgium (Societe des Mines & Fonderies de Zinc de la Vieille Montagne, S.A.), West Germany (Duisburger Kupferhütte, Duisburg, and Unterharzer Berg- und Hüttenwerke G.m.b.H., Goslar), and the U.S.S.R.

Small amounts of thallium have been produced by Cerro de Pasco Corp., at its smelter in La Oroya, Peru, and by Hudson Bay Mining and Smelting Co., Ltd., Flin Flon, Manitoba, Canada.

DEFINITIONS OF TERMS, GRADES, AND SPECIFICATIONS

Thallium is bluish white, malleable, and softer than lead. A freshly cut surface of thallium dulls to a bluish grey tinge when exposed to air, and in a few weeks a thick oxide crust forms. Thallium has an atomic number of 81 and an atomic weight of 204.39. The metal has a density of 11.85 grams per cubic centimeter at 20° C and 11.25 grams per cubic centimeter at 330° C. The element melts at 303° C and boils at 1,457° C. Other physical properties of thallium include (*1*, *5*) [2] latent heat of fusion, 5.04 calories per gram; latent heat of vaporization, 189.9 calories per gram; volume contraction on solidification, 3.23 percent; and tensile strength 1,300 pounds per square inch. Thallium has valences of 1 and 3.

[1] Commodity specialist.
[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

Thallous compounds include the water-soluble acetate, nitrate, perchlorate, hydroxide, sulfate, carbonate, and ferricyanide; the moderately hot-water-soluble halides; and the insoluble sulfide and chromate. Thallic compounds are less numerous and mostly unstable, being readily reduced to thallous salts by stannous chloride, sulfurous acid, metallic thallium, ferrous sulfate and sodium arsenite, or boiling water. Thallium metal dissolves slowly in hydrochloric acid, readily in sulfuric acid, and even more readily in nitric acid.

Thallium forms alloys with antimony, bismuth, cadmium, indium, lead, magnesium, mercury, potassium, sodium, and tin, but most of these alloys are unstable in air. Brittle alloys are obtained with antimony, bismuth, gold, and platinum, and malleable alloys are obtained with copper, lead, and silver.

Thallium metal and compounds have long been known to be toxic (*2–3, 9*). Thallium can be absorbed into the human body by skin contact, by inhaling dusts, fumes, and mists, or by ingestion. The element is not quickly eliminated from the body, and absorption of subtoxic quantities eventually may accumulate to a toxic level. Symptoms of poisoning from thallium compounds include actions similar to those of intoxication, loss of sleep, and various pains throughout the body. Overexposure may result in loss of hair, serious gastrointestinal and nervous system disorders, and sometimes death. A specific antidote for thallium poisoning is not known, but industrial poisonings from thallium are rare because safety procedures have been well established.

Thallium metal is normally sold as sticks or rods with a purity ranging from approximately 99.90 to 99.98 percent thallium. High-purity thallium with a guaranteed analysis of 99.999+ percent is also sold.

TECHNOLOGY

Widely divergent estimates of the abundance of thallium in the earth's crust have been published. In 1947 Ahrens' estimate of 3 grams per ton increased previous estimates by a factor of 10; in 1958 Mason assigned a value of 1 gram per ton to thallium and placed it 58th in a listing of relative abundance of the elements.

Traces of thallium have been found in many minerals, including berzelianite, carnallite, chalcopyrite, dufrenoysite, galena, feldspars, micas, hematite, jordanite, manganite, pitchblende, pyrite, pyrolusite, and sphalerite. Crookesite [$(Cu,Tl,Ag)_2Se$], hutchinsonite [$PbS\cdot(Tl,Ag)_2S\cdot 2As_2S3$], vrbaite [$Tl_2S\cdot 3(As,Sb)_2S_3$], and lorandite [$Tl_2S\cdot As_2S_3$] contain 16 to 60 percent thallium, but these minerals are rare. Thallium is known to occur in arsenical gold ores at Mercur, Utah. Owing to its association with many minerals, thallium is found in tailings, liquors, residues, and dusts resulting from milling and chemical and metallurgical processing of various ores (*11*). The element is also found occasionally in commercial products such as arsenic, bismuth, cadmium, platinum, tellurium, zinc, and sulfuric acid. The trace amounts of thallium found in zinc-bearing ores, along with the normally associated cadmium, indium, and germanium, are concentrated in certain flue dusts and residues which provide the principal commercial source for production of thallium.

Several methods have been developed to extract thallium from ores, flue dusts, and other materials (*1, 4–6, 11*). In one process applied to cadmium- and thallium-bearing flue dust resulting from the smelting of lead-zinc sulfide ores, the dust is leached with sulfuric acid, and cadmium and thallium sulfates are formed. After precipitating most of the impurities as sulfides and hydroxides, the purified solution containing cadmium and thallium sulfates is electrolyzed for deposition of cadmium. When the ratio of thallium to cadmium in the electrolyte reaches 1 to 10, new cathodes are introduced. The electrolysis is continued, and a cadmium-thallium alloy containing 5 to 20 percent thallium is deposited. This alloy is converted to hydroxides by treatment with hot water and steam, and sodium carbonate is added to precipitate the cadmium. The cadmium-free filtrate containing thallium carbonate is then treated with hydrogen sulfide to precipitate thallium sulfide. The washed thallium sulfide is dissolved in sulfuric acid and boiled free of hydrogen sulfide, and the resulting solution of pure thallous sulfate is electrolyzed to recover pure metallic thallium sponge. The sponge is then pressed, melted, and cast.

Thallium metal also can be prepared from thallium sulfate solution by precipitation on zinc plates arranged vertically around the sides of a vessel. After heating for several hours thallium sponge is deposited on the zinc. The spongy mass is separated from the plates, thoroughly washed with water, and compressed or fused into sticks.

Another method uses zinc dust cementation of thallium, cadmium, and indium from a leached solution of pyrite cinders. The cementite is redissolved and converted into a zinc-free mercury amalgam; then by fractional distillation it yields an indium-containing thallium fraction which is further refined to thallium metal.

Production of sulfate, the main commercial product, is obtained by the relatively easy con-

version from the metal. Another method employs leaching and cementation of impurities followed by fractional crystallization of the thallium sulfate.

High-purity thallium is produced by two or more stage electrolysis, amalgam electrolysis, or fractional dissolution and precipitation. Purification can also be obtained by the zone-refining process.

USES

Many uses have been suggested for thallium metal, alloys, and compounds, but there are few applications with a sustained substantial consumption (*1*, *5*, *10–11*). Since 1920 thallium has been best known for its odorless, tasteless, and very poisonous sulfate which is used to exterminate rodents and ants. On rats it acts slowly and cumulatively, principally as a killer; in small doses it halts reproductive processes and thereby restricts the rat population.

There are small but important uses for thallium in electronics. Thallium-activated sodium iodide crystals mounted on photomultiplier tubes are an integral part of certain portable scintillation counters for detecting gamma radiation. The ability of thallium bromoiodide crystals to transmit infrared radiation and of thallium oxysulfide crystals to detect light of this wavelength has been employed extensively in military communications systems.

Low-melting glasses containing arsenic, thallium, sulfur, and selenium are used to coat semiconductors, capacitors, and other electronic devices to protect them from atmospheric oxidation, contamination, and humidity.

Thallium compounds impart black or brown colors and increase the density and index of refraction in glass used in optical instruments and for synthetic gems. Thallium pigments in artists' paints are resistant to hydrogen sulfide. Water solutions of thallous formate or thallous formate-malonate can be used as heavy liquids in the sink-float separation of minerals in laboratory work. Thallium salts absorb traces of oxygen and can be used to increase the life of tungsten filaments in incandescent lamps. Burning thallium salts produce a bright-green flame and have some application in rockets and flares. Thallium salts also have been used as additives to fuels to prevent knocking in internal combustion engines. Thallium has been a constituent in some medicines to treat dysentery, tuberculosis, and scalp diseases, but the narrow margin between toxicity and therapeutic benefits limits its use in this field. It has been used in the catalytic reduction of nitrobenzene by hydrogen.

Thallium alloyed with mercury has been used in low-temperature thermometers; with copper and copper-lead in bearings; with silver in contacts, in bearings, and for articles requiring high resistance to acids and hydrogen sulfide; with lead in solder and fuse metal; with tin and lead as anodes for the electrowinning of copper; and with vanadium as a catalyst in the manufacture of sulfuric acid.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Commercial thallium, along with cadmium, gallium, indium, and germanium is obtained from processing zinc ores for zinc and pyrites for sulfuric acid.

ALTERNATE MATERIALS

Alternative materials are available for most uses of thallium. In exterminating rodents, thallium sulfate can be replaced by other chemicals that are safer to humans and less harmful to desirable animals and birds.

RESOURCES

Resources of thallium are sufficient for this little-used minor metal. Estimates of its principal commercial reserves in sulfide ores have not been published. Mill tailing and unmined arsenical gold ores at Mercur, Utah, are reported to contain large quantities of thallium. Potash deposits contain significant quantities of thallium but are not of commercial importance at present.

SOURCES OF STATISTICAL INFORMATION

Data on domestic production and consumption of thallium are obtained annually by the Bureau of Mines through industry canvasses but are kept in confidence and not published, at the company's request.

PRODUCTION AND CONSUMPTION

Data on domestic production and consumption of thallium are company confidential. Only Belgium, West Germany, the United States, and the U.S.S.R. are known to produce primary thallium metal or sulfate.

TARIFF

Thallium in concentrates can enter the United States duty-free, but the metal and its salts are dutiable at 10.5 percent ad valorem, effective June 30, 1958.

PRICES

The price of thallium metal was $10 per pound prior to 1944, then gradually rose to $20 in 1947. By 1949 the price descended to $12.50 per pound and remained there until December 1957, when it dropped to $7.50 per pound. This price prevailed in 1963 for orders of 25 pounds or more.

The price of thallium sulfate in 1963 ranged from $5 per pound for orders of 100 pounds or more to $10 per pound for orders of less than 10 pounds.

High-purity thallium is priced at $3 per 25 grams.

TAXES

No special taxes are imposed on the thallium industry. Depletion allowance for domestic producers of thallium metal is 15 percent.

RESEARCH

Production research has been conducted by companies to develop metallurgical procedures for the recovery of thallium from zinc-processing operations. A spectrochemical method for determining thallium in source materials was developed by the Bureau of Mines. In response to the increased demand for thallium in military and peaceful applications, the Bureau made a nationwide search for sources of thallium in 1947–49. White arsenic and Cottrell preciptator dusts from the American Smelting and Refining Company plant at Murray, Utah, were found to be the most promising sources of thallium (*8*). A Bureau report on determining thallium in source materials was published (*7*).

Through research, the U.S. Department of Agriculture found that the possibility for secondary poisoning of birds and animals through eating carcasses of rodents killed by thallium sulfate was very small.

Contributing to utilization research, the Bureau of Mines investigated the use of thallous silver nitrate and thallous formate in water to separate minerals by sink-float methods for use in mineralogical analysis, and also developed methods of preparing and cleaning thallium-base liquids used in sink-float testing of minerals. Thallous formate and thallous malonate-formate were among the materials studied.

Recent development in lamps that produce radiation in the erythemic (suntan) range has included investigation of thallium-activated alkaline earth silicates and phosphates which provide the desired radiations. Use of thallium in mercury vapor lamps to produce a very white light has been investigated. Substantial research has been conducted on improved methods of producing thallium-containing crystals and their electronic applications.

OUTLOOK

Thallium consumption is expected to remain fairly constant, and thallium will be used predominantly for rodenticides. Some of the lesser applications may show increased consumption but this will not greatly affect the total. Should demand increase for thallium, resources and productive capability are available to quickly expand the supply.

PROBLEMS

The principal problem for thallium is lack of uses and demand for the metal and its alloys and compounds. Many of the chemical and physical properties of thallium are known; but fuller knowledge of the properties may lead to development of larger usage of the element. The principal use as a rodenticide is vulnerable to substitution by other chemicals that are less expensive or less dangerous to humans and desirable birds and animals.

In some uses that have been developed for thallium, either its toxicity or its relatively high price is a deterrent.

Resources are ample for anticipated demand, but should a sudden large use for thallium develop, a problem of economic supply could result because thallium is a byproduct of base metals and the supply is therefore inflexible.

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THORIUM

By Charles T. Baroch [1]

THORIUM has the nuclear property shared with uranium 238 of being transmuted under neutron bombardment into uranium 233 which is fissionable in a chain reaction. Thus it is a potential fuel for the generation of nuclear energy.

The element thorium is widely distributed, comprising from 0.001 to 0.0015 percent of the earth's crust. It is usually associated with uranium or the rare-earth elements and is obtained commercially principally from monazite, thorianite, and thorite. Large deposits of monazite occur as beach sands in India, Brazil, Malaysia, and the southeastern coast of the United States. Thorianite and thorite occur with uranium in Idaho, Colorado, Ontario, and the Malagasy Republic, and increasing amounts of thorium are being derived as coproducts of uranium.

Monazite is recovered from beach sands by gravity concentration and electrostatic and electromagnetic methods. The concentrates are processed by wet chemical methods using either hot sulfuric acid or strong sodium hydroxide solution to decompose the monazite. Other chemical processing with selective precipitation and filtration yields a crude thorium nitrate solution that is purified by solvent extraction.

Thorium contained in dilute solution from the uranium treatment plant of Rio Tinto Dow, Ltd., at Elliot Lake, Ontario, Canada, is recovered by solvent extraction. The crude precipitate, containing 15 to 20 percent thorium, is refined to metallurgical-grade thorium oxide. Thorium metal is produced by the reduction of thorium halides or oxide by alkali or alkaline-earth metals, by thermal decomposition of the iodide, or by electrolytic methods.

Thorium nitrate is used for producing incandescent gas mantles, and the oxide is used as a refractory, as a catalyst, for producing a dispersion-hardened nickel alloy, and in nuclear breeder reactors for the production of uranium 233. Thorium metal also is used in nuclear breeder reactors and as an alloying agent, particularly with magnesium.

Thorium has a great potential use as a source of energy if a successful breeder reactor can be developed in which surplus neutrons in the fission of either plutonium, uranium 233, or uranium 235 are captured by thorium to produce uranium 233. Substantial research on the thorium-uranium 233 fuel recycle technology has been done, but much more remains. Until a breeder reactor is developed, only experimental quantities of thorium will be used for nuclear purposes.

The principal technical problems are the development of new uses and of process improvements that would lower the cost of thorium products. The main economic problem is the development of a larger market commensurate with the abundance of thorium resources.

BACKGROUND

Thorium was discovered by the Swedish chemist Baron Jons Jakob Berzelius in 1828 in a mineral now called thorite. Little use was found for thorium until 1885, when Dr. Carl Auer von Welsbach of Vienna discovered that thorium oxide became incandescent when heated. From this discovery he developed the Welsbach mantle which was widely adopted in gaslighting and later for gasoline and kerosine lamps.

Thorium derived from monazite was produced as early as 1893 in the Carolinas; however, this production was soon eclipsed by production from Brazil which started in 1895. Production from India began in 1911. At the same time, German manufacturers soon built up almost a complete monopoly of the thorium nitrate industry. World War I cut off German supplies and enabled domestic production of thorium nitrate to expand, although monazite

[1] Commodity specialist.

supplies still came from India and Brazil at prices so low that domestic producers could not compete. In the early 1920's electricity began to supplant gas for general lighting purposes and the need for thorium mantles declined; however, rare-earth elements began to be used increasingly, and thorium became a byproduct of the rare-earth elements.

The discovery of the principles of fission and the development of the nuclear bomb was followed by the discovery in 1946 that Th^{232} could be transmuted into U^{233}, a fissionable isotope. India in 1947 and Brazil in 1951 nationalized the production of monazite for their own use, and this jeopardized the domestic supply. Large domestic resources were found, and the rich monazite mine at Steenkampskraal, Republic of South Africa, began production in 1953 and became a major producer, stabilizing the market. This mine was closed in 1963, when developed ore was depleted.

Meanwhile, a new source of thorium began production in 1959 when the Elliot Lake plant of Rio Tinto Dow, Ltd., in Ontario, Canada, began recovering thorium from waste uranium-plant solutions. If demand increases, additional thorium could be recovered as long as uranium production is maintained. About 1960, the French Atomic Energy Commission also began producing thorium for its own use from both uranothorianite and monazite in Malagasy Republic.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Prior to the production of thorium in Canada as a byproduct of uranium, most of the thorium was derived from monazite and was coproduced with the rare-earth elements. Some monazite was recovered as a byproduct from Florida beach sands by Titanium Alloy Manufacturing Division, National Lead Co., but most monazite was imported from the Republic of South Africa. More recently some monazite has been imported from Malaysia, Ceylon, and Australia.

Processing of monazite was pioneered by Lindsay Light Co., established in 1902, which was changed to Lindsay Light & Chemical Co. in 1935, and which merged in 1958 with American Potash & Chemical Corp. as the Lindsay Chemical Division. This firm, with its plant at West Chicago, Ill., retains its dominant position as a processor of thorium-bearing ores and concentrates and produces high-purity rare-earth and thorium compounds. Other processors of ores and concentrates are Nuclear Fuel Services, Inc., formerly Davison Chemical Division of W. R. Grace & Co., Erwin, Tenn.; and Vitro Chemical Co., Chattanooga, Tenn. Nuclear Fuel Services specializes in thorium metal and oxide, and Vitro produces thorium-magnesium master alloy, and thorium nitrate and hydroxide.

Rio Tinto Dow, Ltd., was formed by The Rio Tinto Mining Company of Canada, Ltd., and Dow Chemical of Canada, Ltd., a subsidiary of the Dow Chemical Co., for recovering crude thorium sulfate cake from Rio Algom's Nordic mill at Elliot Lake, Ontario, Canada. Part of the cake is refined to metallurgical-grade thorium oxide at the Quirke plant nearby, and the rest goes to Dominion Magnesium, Ltd., at Haley, Ontario, for the production of pure thorium-metal pellets, thorium powder, and thorium-magnesium master alloy. This group of Canadian operations has a designed capacity for 150 to 200 tons of thorium annually.

Westinghouse Electric Corp., Bloomfield, N.J., manufactures thorium metal and a special grade of thorium oxide from metallurgical-grade thoria, for use in lamp filaments and emission material. Fabricators of uranium reactor fuels also have capabilities for processing thorium fuels. Among these are The Babcock & Wilcox Co., Lynchburg, Va.; General Atomic Division, General Dynamics Corp., San Diego, Calif.; Kerr McGee Oil Industries, Inc., Cushing, Okla.; Metals & Controls, Inc., a division of Texas Instruments, Inc., Attleboro, Mass.; National Lead Co., Albany, N.Y.; Nuclear Fuel Services, Inc., Erwin, Tenn.; Nuclear Materials & Equipment Corp., Apollo, Pa.; United Nuclear Corp., Hematite, Mo.; and Westinghouse Electric Corp., Pittsburgh, Pa.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

The element thorium, chemical symbol Th or isotopic symbol Th^{232}, has an atomic weight of 232.05, atomic number 90, and lies in the fourth subgroup of the Periodic Table with titanium, zirconium, and hafnium. It is mildly radioactive with a half-life of 1.39×10^{10} years, decaying through 12 intermediate radioactive isotopes, finally yielding a stable isotope of lead, Pb^{208}.

Th^{232} is not fissionable in itself but is a *fertile material;* that is, by irradiating it with slow neutrons, it is converted into Th^{233} which is highly radioactive with a half-life of 23 minutes and decays to protactium, Pa^{233}, with a half-life of 27.4 days, which in turn decays to uranium 233 (U^{233}). U^{238} is a similar fertile material that will produce plutonium, Pu^{239}, by neutron bombardment. Both U^{233} and Pu^{239} are artificial elements and are fissionable. The production of fissionable material from fertile material is

known as *breeding*, and a nuclear reactor that produces more fissionable material than it consumes is called a *breeder reactor*.

When the atomic nuclei of fissionable atoms are struck by neutrons of proper energy (speed), the nucleus splits into two atoms of nearly equal size. This reaction is called *fission* and results in the release of a large amount of energy.

The products of fission are *fission fragments*, and an average of 2.5 neutrons are produced for each atom fissioned. These released neutrons make a *chain reaction* possible, as these new neutrons can cause fission in other nearby fissionable atoms. A *nuclear reactor* is a device containing fissionable materials and control devices that can absorb excess neutrons, yet permit sufficient neutrons to fission other nuclei at a controlled rate.

No general specifications for thorium metal or compounds have been established. Producers manufacture various grades of their products that are suited for the various uses, and they will further refine materials as needed for special purposes.

Metallurgical-grade thorium oxide is better than 99.8 percent ThO_2. For nuclear uses, a better grade product is usually required by specifications established by each reactor manufacturer. Reactor-grade material, either oxide or metal, must be 99.9 percent pure and must be especially low in high-neutron-absorbing elements, such as boron, cadmium, gadolinium, samarium, dysprosium, and europium, which must be well below 1 part per million; most other metallic impurities must be below 50 parts per million.

Thorium-magnesium master alloy, sometimes referred to as magnesium-thorium hardener, is used for producing magnesium alloys, and contains from 20 to 40 percent Th.

Thorium nitrate as made by modern solvent-extraction methods is a very pure material and is used as an intermediate product for the production of oxide or metal. One large manufacturer produces four grades of thorium nitrate, in addition to the mantle-grade which contains from 0.5 to 1.0 percent sulfate, SO_3, intentionally added because it gives a very hard, dense ash and strengthens the mantle.

TECHNOLOGY

Mineralogy and Geology

Thorium is widely distributed in nature and is usually associated with uranium and the rare-earth elements. Its geochemical abundance is estimated to be between 10 to 20 parts per million in the earth's crust, about three times that of uranium.

Monazite has been the most important thorium-bearing mineral in the past. It is essentially a phosphate of the rare-earth elements but contains up to 12 percent ThO_2 and up to 1 percent uranium oxide (U_3O_8). Typical analyses of monazite sands from different sources are as follows, in percent (*13*) :[2]

	ThO_2	Rare-earth oxides	U_3O_8
India	8.9	59.4	0.35
Brazil	6.5	59.2	.17
United States	3.1	40.7	.47
South Africa, Republic of	5.9	46.4	.12
Malagasy Republic	8.8	46.2	.41

Monazite has a specific gravity of 5.0 to 5.3 and a hardness of 5 to 5.5 on the Mohs' scale. It occurs widespread as small accessory grains and crystals in granites, gneisses, and syenites, occasionally in large masses and crystals. Weathering of these rocks and water action concentrates the monazite in placer deposits along river beds and beaches. The most important deposits occur in India and Brazil, and others are found in Australia, Ceylon, Indonesia, Malagasy Republic, Malaysia, Republic of South Africa, Canada, and the United States. Important domestic deposits have been worked in Florida and South Carolina where monazite was recovered as a byproduct of ilmenite, and in Valley County, Idaho, where it occurs with euxenite. Other deposits are known in North Carolina, Michigan, and California. Pegmatite occurrences are at Amelia, Va.; Spruce Pine, N.C.; Gunnison and Chaffee Counties, Colo.; Portland, Conn.; Glorieta, N. Mex.; and the Aquarius Range, Ariz. (*6*).

The Steenkampskraal deposit, 50 miles north of Van Rhynsdorp, Cape Province, Republic of South Africa, is a hydrothermal vein of fine-grained quartz and monazite in Precambrian granitic rocks. The vein is from a few inches to 6 feet thick and was exposed for 600 feet. Ore as rich as 75 percent monazite was found, but most of it was only 20 percent. Ore contained up to 5 percent copper.

The two principal India beach deposits are in Travancore at Malavalakurichi and near Chavara on the southwest coast extending from Quiton to Cape Comorin. Other lower grade deposits are in the Malabar district north of Travancore and on the east coast in Madras and Orissa. The black sands constitute less than 1 percent of the beach sand, and they contain from 40 to 50 times more rutile and ilmenite than monazite (*10*).

The Brazilian beach deposits are in the States of Bahia, Rio de Janeiro, and Espirito Santo.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

Heavy minerals range from a few percent to 75 percent of the beach sand and the black-sand portion from Prado, Bahia, contained 18 percent monazite, 59 percent ilmenite, 2 percent rutile, and 21 percent zircon.

Monazite occurs in beach and dune deposits near Fort Dauphin, Malagasy Republic. The sands average 2 to 2.5 percent monazite and total about 50 percent heavy minerals.

Thorianite, ThO_2, and thorite, $ThSiO_4$, are the only two true thorium minerals and both may have varying amounts of UO_2 and UO_3 replacing ThO_2. Thorianite is isomorphous with uraninite and may contain up to 90 percent ThO_2 and up to 33 percent U_3O_8. When U_3O_8 content is above 15 percent, the mineral is called uranothorianite. Thorite may contain up to 80 percent ThO_2 and up to 25 percent U_3O_8. When it contains more than 5 percent U_3O_8 it is called uranothorite.

Important thorianite deposits occur in pyrometasomatic veins in the Bancroft Region, Ontario, Canada, and near Fort Dauphin, Malagasy Republic. It has been found in small quantities in sand and gravel deposits in Alaska, California, Ceylon, Montana, New Zealand, and other places. Uranothorianite in the Malagasy Republic is in masses and lenses of pyroxenite which contains from 0.3 to 0.4 percent uranothorianite ranging from 57 to 83 percent ThO_2 and 8 to 26 percent U_3O_8.

Thorite is found in pegmatites, carbonatites, veins, and placers, also as an accessory mineral in many igneous rocks. Notable deposits of thorite occur in the Wet Mountains of Custer County, and other places in Colorado, as veins in a Precambrian complex of gneisses and quartzite; and in the Lemhi Pass district along the Idaho-Montana line as quartz-hematite-copper fissure veins from a few inches to 10 feet wide and as much as 500 feet long. Thorite also occurs in beach sands in New Zealand and central California and in gold placers along the Tuolumme, Cosumes, and other rivers. Lesser deposits are found in North Carolina, Texas, Australia, Norway, and Japan.

Mining, Milling, and Processing (3)

Monazite is recovered from river and beach sands by placer mining methods, most often using bucket or suction dredges, but sometimes using shovels or draglines and, in primitive mining operations, hand shovels. Tables, jigs, and Humphreys spirals are used to make a bulk concentrate of the heavy minerals, known as black sands. This concentrate is usually transported to another plant for intensive treatment to separate the various components into marketable products. Monazite is usually a minor component and other heavy minerals present may include magnetite, ilmenite, rutile, zircon, cassiterite, garnet, staurolite, and others.

Black sands, after drying, are separated by magnetic separators and electrostatic separators, varying combinations being used for sands with different constituents. In the Malagasy Republic, for instance, ilmenite is removed first with a low-intensity magnetic separator, and the monazite is removed with high-intensity magnetic separators, leaving the nonmagnetic zircon. A plant in Brazil uses first an electrostatic separator that separates the electrical conducting minerals, ilmenite and rutile, from the nonconductors, monazite and zircon. Electromagnetic separators then separate the magnetic ilmenite and monazite from the nonmagnetic rutile and zircon.

Monazite is treated by a fairly complex series of chemical-processing methods to separate thorium from a predominant quantity of rare-earth elements and phosphate. Initial treatment is either with hot concentrated sulfuric acid or hot concentrated sodium hydroxide solutions.

Sulfuric acid digestion produces a sulfuric acid-phosphoric acid solution of the rare-earth elements, thorium, uranium, and other impurities, which is filtered from the gangue, primarily silica. Thorium usually is separated from this solution by precipitation, but fractional crystallization also has been used. Partly neutralizing the acid to pH 1.0 with ammonium hydroxide gives almost complete recovery of the thorium as phosphate, and only about 5 percent of the rare-earth elements as sulfates. The rare-earth elements are recovered by further alkalization of the solution. The crude thorium phosphate precipitate is dissolved in nitric acid and the thorium is recovered by solvent extraction (7).

Digestion of monazite with sodium hydroxide (50 percent NaOH at 140° C) solubilizes the phosphate, leaving hydrous oxides of thorium, uranium, and the rare-earth elements after filtration. This residue is dissolved in hydrochloric acid, and then the solution is neutralized carefully with sodium hydroxide. All thorium and uranium are precipitated with only a small quantity of the rare-earth elements. This crude thorium hydroxide is dissolved in nitric acid and purified by solvent extraction, as with the crude thorium phosphate precipitate from the acid process.

A modification of the acid process was developed at Ames Laboratory, Iowa State College. Thorium and the rare-earth elements were precipitated from the diluted sulfate solution with sodium oxalate, leaving uranium to be recovered on an anion exchange resin. The oxalate precipitate was treated with sodium hydroxide,

leaving a hydroxide precipitate and regenerating sodium oxalate. The hydroxides were calcined to decompose residual oxalate and produce oxides which could then be dissolved in nitric acid for purifying the thorium by solvent extraction.

Solvent extraction is an efficient method of separating and purifying thorium, and it has superseded all other methods. Several variations of the method have been developed for different conditions. Typically, the nitric acid solution of thorium, containing rare-earth elements, uranium, and other impurities, is brought vigorously into contact with an organic solvent, such as kerosine or xylene, which is insoluble in water. The solvent contains an organic compound, like tributyl phosphate (TBP), which forms a complex compound with thorium. The thorium complex dissolves in the solvent phase leaving the impurities in the aqueous phase. After separating the two liquids, the thorium is stripped from the solvent by mixing violently with a dilute 0.02-normal nitric acid solution, thereby bringing the thorium back into a new aqueous phase. The high-purity thorium nitrate product may be crystallized from this aqueous phase or precipitated as an oxalate for further processing (*4*).

The thorium-recovery plant of Rio Tinto Dow, Ltd., near Elliot Lake, Ontario, receives the waste solution from the uranium mill of Rio Algom Mines, Ltd. This contains about 1 pound of thorium per thousand gallons and was formerly discarded to the tailings pond. Thorium is extracted by solvent extraction, and the organic extractant is stripped to form a precipitate containing from 15 to 20 percent Th. The precipitate is either refined into metallurgical-grade thorium oxide or is used to produce thorium metal or thorium-magnesium master alloy.

Thorium and yttrium are recoverable from thorite ores by leaching with sulfuric acid. Thorium was removed from the leach solution by solvent extraction using a kerosine organic phase containing 10 percent primary alkylamine and 10 percent isodecyl alcohol. The thorium was stripped from the organic solvent by a 2-molar ammonium carbonate solution. Yttrium was recovered from the thorium-free acid leach solution by solvent extraction in a solvent containing 0.24-normal di-2-ethylhexyl phosphoric acid (EHPA) in kerosine. The organic solvent was stripped of yttrium with 6-normal hydrochloric acid (*2*).

Thorium oxide is prepared by calcination of thorium oxalate precipitated from the pure nitrate solution derived from solvent extraction.

Reduction and Refining (*8*)

The production of pure thorium metal is very difficult as it is very reactive and has a high melting point (1,840° C). It is prepared by reduction of the halides with calcium or magnesium, reduction of thorium oxide with calcium or sodium, fused-salt electrolysis, or thermal decomposition of thorium tetrachloride by the Van Arkel-de Boer process (*14*).

The U.S. Atomic Energy Commission (AEC) plant at Fernald, Ohio, operated by National Lead Co. used a process developed at the Ames Laboratory for producing about 20 tons of thorium per month. Thorium fluoride, prepared from ThO_2 with anhydrous hydrofluoric acid, was mixed with anhydrous zinc chloride and reduced with metallic calcium in a steel bomb. The bomb was heated to about 650° C when the reaction proceeded by its heat of reaction. Part of the zinc chloride was reduced along with the thorium fluoride, producing a zinc-thorium alloy with a low melting point. After separating the calcium chloride slag, the alloy was heated in a vacuum to remove the zinc, leaving a thorium metal sponge. The sponge was melted to a solid ingot by arc melting in a water-cooled copper crucible using a consumable electrode of the thorium metal sponge.

Thorium also has been produced by metallothermic reduction of thorium tetrachloride by sodium, potassium, calcium, and magnesium. Magnesium reduction is similar to the Kroll process for producing titanium and zirconium (*5, 11*).

Westinghouse Electric Corp. produced thorium powder by reacting thorium oxide with a slight excess of calcium in a refractory-lined steel bomb heated to 950° C. The product was leached with dilute acetic or nitric acid, and the thorium powder was dried in a vacuum, followed by compacting and sintering. Metal produced in this manner had a purity of 99.8 percent.

Thorium is too reactive to be deposited electrolytically from aqueous solutions, but it has been prepared on a small scale by electrolysis of the oxide, fluoride, and chloride in molten-salt electrolytes. The oxide can be electrolyzed in either a potassium-thorium fluoride mixture and in a sodium-potassium-thorium chloride bath. The fluoride was electrolyzed in an electrolyte of a double fluoride of thorium and potassium and sodium chloride in a pilot plant in 1952, but fluoride accumulated in the bath and it could not be run continuously. Electrolysis of thorium tetrachloride proved to be better, as chlorine was released at the anode continuously. Electrolysis produces thorium powder.

USES

The most important use for thorium metal is in magnesium alloys. A typical alloy contains 96.3 percent magnesium, 3 percent thorium, and from 0.5 to 0.7 percent zirconium. Heat treatment gives the alloy extraordinary resistance to creep and excellent strength up to 750° F. Their light weight and high-temperature strength make these alloys particularly suitable for structural use in high-speed aircraft and missiles. They can be rolled, deep drawn, extruded, spot welded, and fusion welded by the inert-arc process. Standard sheet and plate are available.

Thorium nitrate is of great importance in the fabrication of incandescent gas mantles, millions of which were used by the Armed Forces during World War II and which are still used in large quantities. For camping and outdoor use, gas mantles provide efficient and portable light from kerosine or gasoline lamps. Mantles are made from cotton, ramie, or synthetic fibers woven into cloth and impregnated with thorium nitrate (25 to 50 percent) solution containing 1 to 2 percent of cerium nitrate, then dried and denitrated with ammonia, hydrofluoric acid, or alkali fluoride solution, converting the thorium and cerium to insoluble hydroxides or fluorides. When the cloth burns away a skeleton of thoria remains, which when heated gives a brilliant white light. Mantle manufacturers prefer thorium nitrate containing about 0.6 percent sulfate, SO_3 which, it is claimed, strengthens the ash skeleton of the mantle (*9*).

Thoria has a melting point of 3,220° C, is the most stable of the refractory oxides, and has a low dissociation pressure. However, it has poor resistance to shock and it does not have high strength. These disadvantages and its high cost permit it to be used only in some very specialized crucibles, such as for the melting of molybdenum, columbium, nickel, and similar metals or alloys.

Nickel containing about 2 percent thorium oxide dispersed throughout produces an alloy that has superior strength and corrosion resistance at temperatures as high as 2,400° F. It will outperform columbium and most other superalloys at long-time low-load service. Made and sold under the trade name, TD Nickel, it consists of a very fine-grained nickel-thoria powder produced by chemical methods and compacted by powder-metallurgy methods. It can be worked with conventional metal-forming machinery and is finding applications in rockets, space vehicles, and chemical and furnace parts (*12*).

Thorium oxide is used as a catalyst in the petroleum and chemical industries, particularly to convert ammonia to nitric acid and sulfur dioxide to sulfur trioxide and sulfuric acid. A small amount of thoria is compounded with tungsten to produce filaments for incandescent lamps. From 0.8 to 1.2 percent thorium oxide makes the filaments more ductile and inhibits crystallization of the tungsten, thereby keeping the filament from getting brittle. Thoriated tungsten also shows an improved thermionic emission, making such filaments highly desirable in electronic tubes. Metallic thorium also requires comparatively little energy to produce high electron emission and serves well as electrode material in gaseous discharge lamps and mercury arc lamps. As metallic thorium emits strong monochromatic radiation, it is used as target material in X-ray tubes. Thorium oxide is used in fabricating thoriated tungsten electrodes for inert-arc welding and as nonconsumable electrodes in arc melting of transition metals. From 1 to 2 percent thoria offers the advantage of instant starting and arc stability.

Thorium is a fertile material and probably will become an important nuclear fuel. It can be converted in a nuclear reactor to uranium 233, which is fissionable and can sustain a chain reaction. In a breeder reactor, the system thorium-uranium 233 gives promise of complete utilization of thorium in the production of nuclear power. The energy available from the world supply of thorium has been estimated to be greater than the combined energy available from uranium, coal, and oil resources.

Thorium test reactors have been designed using thoruim as metal, dioxide, fluoride, and carbide. The trend appears to be toward ceramic elements that favor ThO_2 or ThC pellets, except in the molten-salt reactor concept, which uses ThF_4 in mixed lithium and beryllium fluoride. Thorium oxide also has been used as a coating for spherical UO_2 pellets for use in either fixed- or fluidized-bed reactors (*8*).

Initially, breeder reactors will require either U^{235} or Pu^{239} to provide the neutrons necessary to transmute Th^{232} to U^{233}, but once sufficient U^{233} becomes available, reactors can operate on a Th^{232}–U^{233} cycle and will need only thorium for the replacement of consumed fuel. While the thorium-uranium cycle produces a higher breeding ratio than the uranium-plutonium breeder, it has the disadvantage of also producing uranium 232 which is not fissionable and which decays into a series of short-lived daughter products. These emit penetrating gamma rays and necessitate remote-control of all fabrication.

The following three power reactors have been designed and operated with thorium:

1. The Consolidated Edison Co. of New York pressurized-water reactor at Indian Point, N.Y.,

has an electrical capacity of 255 megawatts. The original reactor core contained 38,000 pounds of ThO_2 mixed with 2,600 pounds of UO_2 enriched to 93 percent U^{235}. The second core was redesigned to use enriched uranium and U^{238}, largely because of its lower cost.

2. The Elk River Reactor, Elk River, Minn., cooperatively built by AEC and Rural Cooperative Power Association, started up in 1963 and has a capacity of 20 megawatts. It is of the boiling-water type, and its core consists of about 8,500 pounds of thorium and 800 pounds of enriched uranium.

3. The Peach Bottom, Pa., reactor of Philadelphia Electric Co., capacity 40 megawatts, was put in full operation in 1964. It is a gas-cooled, graphite-moderated reactor designed to operate at the high temperatures of 660° F inlet and 1,380° F outlet, whereas the other reactors operate at 490° to 550° F. The fuel elements are UC_2, ThC_2, and graphite made into rods.

Among smaller test reactors that have been considered for thorium reactor-fuel experiments are the Sodium Reactor Experiment (SRE), Santa Susana, Calif., an aqueous homogeneous type (HTR) at Oak Ridge National Laboratory, the Liquid Metal Fueled Reactor with a suspension of thorium in a liquid metal (bismuth), the aqueous homogeneous reactor concept using a slurry of UO_2 in heavy water surrounded by a blanket of ThO_2 pellets, and the molten-salt reactor with enriched UF_4 in LiF-BeF_2-ZrF_4 salt with a blanket of ThF_4 in the same type of salt.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Monazite from sand deposits is largely a byproduct of ilmenite, rutile, and zircon production. Further processing of monazite yields rare-earth elements and thorium as coproducts, together with lesser quantities of uranium and yttrium. Copper was a coproduct of monazite from the vein deposit in South Africa. Thorium and uranium are coproducts in many uranothorite and uranothorianite ores, and thorium occurs in small amounts in many uranium ores, often in recoverable quantities such as in the Blind River area of Ontario.

ALTERNATE MATERIALS

No satisfactory alternative materials are suitable for the larger nonenergy uses of thorium, particularly in gas mantles and in alloys. Zirconium and titanium are superior to thorium as a getter in electronic tubes. Beryllia and yttria can often be substituted for thoria as a refractory above 2,000° C.

Uranium breeder reactors are competitive, to a certain extent, with thorium breeder reactors. Neither has been sufficiently developed to predict which will find greatest use.

RESERVES

Known thorium resources of the types that have been mined recently are listed in table 1. In almost all cases individual deposits have been only partially explored and evaluated, and the totals embrace deposits of several distinct kinds, the grades of which cover a wide range. Hence, the data are classed as resources, rather than as reserves. The economic mining of many of the deposits is dependent on recovering and marketing of coproducts, such as ilmenite, rutile, and zircon.

Domestic reserves consist of thorite vein deposits in Idaho and Montana, that have been evaluated by some at 100,000 tons of ThO_2 recoverable, and monazite sands in the Southeastern and Western States.

Canadian reserves are associated mostly with uranium ore in the Blind River and Bancroft region.

Brazilian beach sands were once a source of imported monazite until Brazil imposed an embargo on its exportation. These are in the districts of Espirito Santo, Bahia, and Rio de Janiero. In addition to the figure shown, about 130,000 tons of thorium is estimated to be present in the low-grade (0.07 per cent ThO_2) pyrochlore carbonatite at Araxa in Minas Gerais, which might be recoverable as a byproduct in the recovery of the columbium.

TABLE 1.—*World resources of thorium*

Country	Content, thousand tons ThO_2	Principal types of deposits [1]
India	250	P
Canada	200	S, R
United States	100	V, P
U.S.S.R. and Eastern Europe	100	
Brazil	30	P, R
West Africa	15	P, R
Australia	10	P, R
Malagasy Republic	10	P, R
Nyasaland	10	P
South Africa, Republic of	10	V

[1] P, placer deposits; V, veins; R, concentrations in igneous and metamorphic rocks; S, concentrations in sedimentary rocks.

Source: U.S. Geological Survey Bulletin 1204.

India was another source of monazite for the United States until exports were prohibited. The estimated thorium reserve shown in table 1 is probably conservative. An additional 250,000 tons of ThO_2 may possibly be found in the unexplored inland placers of Bihar and West Bengal.

The uranothorianite deposit at Belafa is the only one being exploited in the Malagasy Re-

public. Even though exploration of this ore body is not complete, reserves are estimated to total 2,500 to 5,500 tons of mineral containing 1,300 to 3,250 tons of ThO_2 and around 1,000 tons of U_3O_8. The balance of the reserve shown in table 1 is in monazite sands at Antete and Fort Dauphin. Another estimate of these sands accounts for about 150,000 tons of monazite at 7.8 percent or about 12,000 tons of ThO_2.

The quest for radioactive materials begun in 1944 included thorium as well as uranium, and all known domestic resources of thorium were examined and evaluated. The magnitude and sources of the reasonably assured total domestic resources are listed in table 2. While most of this thorium is far beyond utilization under present economic conditions, the eventual development of thorium breeder reactors and a strong demand could bring many of these resources into production. Even group 4 has to be regarded as a potential energy source for the far distant future when fossil fuels and uranium can no longer supply the demand.

TABLE 2.—*Magnitude and sources of thorium in the United States*

Group [1]	Price range per pound of ThO_2	Reasonably assured resources of ThO_2 (thousand short tons)	Estimated total resources of ThO_2 (thousand short tons)
1	Under $10	100	400
2	$10–$30	100	200
3	$30–$100	7,000	35,000
4	$100–$500	1,000,000	3,000,000

[1] Group 1. Measured, indicated, and inferred ores, plus geological estimate of potential discoveries; mainly Idaho vein and Altantic States placer deposits.
Group 2. Mainly low-grade placer and vein deposits.
Group 3. New Hampshire (Conway) granite (to a depth of 2,000 feet).
Group 4. Other granites (to a depth of 2,000 feet) extending over large areas of other States.

Source: AEC, Civilian Nuclear Power, a Report to the President, 1962, as presented to the Joint Committee on Atomic Energy, 88th Cong., Feb. 20 and 21, 1963.

Thorium content of the earth's crust is three to four times that of uranium; however, uranium deposits have been formed in higher concentrations, and unit cost would have to increase appreciably before thorium would be equal in availability to uranium. Practically all granites contain thorium and uranium that can be recovered. The Conway granite in New Hampshire represents one of the largest, and it has been examined quite thoroughly, even to metallurgical tests. The outcrop areas total about 300 square miles, and the rock averages about 50 parts per million ThO_2, of which from 60 to 85 percent is recoverable; uranium content averages about 11 parts per million, of which about 56 percent on the average can be recovered. Estimated recovery costs of combined uranium and thorium from different areas of the Conway granite range from $38 to $75 per pound.

The fourth group consists largely of granites in Colorado, California, Idaho, Montana, Texas, and Washington which contain from 40 to as low as 12 parts per million thorium and less than 10 parts uranium. These can be processed at an estimated cost of from $120 to $470 per ton of combined thorium and uranium.

Fuel Value of Thorium Resources

The total energy contents of the domestic thorium resources listed in table 2 are shown in table 3. For comparison, the known recoverable and marginal and undiscovered marginal resources of coal were estimated at 4,220 billion tons with an energy value of 88.6 Q and the energy value of petroleum, natural gas, natural gas liquids, oil in bituminous rock, and shale oil were estimated at an additional 41.5 Q, or a total energy value for all fossil fuel of 130.1 Q.

The total Q value shown in table 3 for reasonably assured resources of thorium is 63,712 Q and for total resources is 192,238 Q. This compares with comparable Q values for uranium of 30,696 Q and 121,490 Q, respectively. Domestic energy consumption in 1963 was about 0.048 Q and world energy consumption was about 0.17 Q. Domestic future use of energy in 1980 is estimated at about 0.082 Q and for the year 2000 it is expected to double this figure.

TABLE 3.—*Energy content of domestic thorium resources* [1]

Group	Thorium resources price range per pound ThO_2	Fission energy content, Q [2]	
		Reasonably assured resources	Total resources
1	Under $10	6	25
2	$10–$30	6	13
3	$30–$100	700	2,200
4	$100–$500	63,000	190,000

[1] See table 2 for quantities of fuel.
[2] Q=1 quintillion British thermal units, or 10^{18} Btu. 1 short ton ThO_2 will produce 6.3×10^{13} Btu on conversion to U^{233} and its complete fissioning.

Source: AEC, Civilian Nuclear Power, a Report to the President, 1962, app. II, p. 34.

SOURCES OF STATISTICAL INFORMATION

Annual data on production, stocks, and shipments of thorium minerals are obtained from producers by the Bureau of Mines. Annual

data on consumption and production of thorium products and their field of use are obtained from processors and consumers. However, much data must remain confidential because of the limited number of producers. World production of monazite is obtained through the Department of State and is reported in the Bureau of Mines Minerals Yearbook, volume I, in the Rare-Earth Minerals chapter; however, the thorium content is not reported. U.S. imports and exports are obtained from the Bureau of the Census, but again the thorium content of monazite is not known.

PRODUCTION, CONSUMPTION, AND TRADE

Thorium is classified as a fissionable source material in the Atomic Energy Acts of 1946 and 1954, and thorium production was classified information from 1945 to 1955. Recognizing its fissionable potential, India banned exports of monazite concentrate in 1946, and Brazil did the same in 1951. Shipments of thorium-bearing materials from Australia and the Republic of South Africa are under Government control.

World production of monazite concentrates by countries is shown in table 4. The thorium content of monazite production is not recorded and varies widely from about 4 percent to 8 percent, usually, with occasional shipments analyzing as high as 12 percent.

Thorium is produced in Canada as a byproduct of uranium processing, but production data are confidential because there is only one producer. Imports until 1962 were classified with barium, boron, strontium, and vanadium metals. In 1963, 5,420 pounds of thorium metal valued at $55,187 was imported into the United States from Canada. Other imports included about 1,300 pounds of thorium nitrate from Canada and the United Kingdom.

Thorium exports were classified by the Bureau of the Census in 1960 into class 6255.0, thorium ores, concentrates, and compounds, and class 6257.0 thorium metal and thorium-bearing alloys including semifabricated and fabricated forms, except special nuclear materials. Data for 1961–63 are shown in table 5.

Ores and concentrates are duty free. The duty rate established August 31, 1963, for metal was 12.5 percent ad valorem, for alloys it was 15 percent, and for nitrate and other compounds 35 percent.

TABLE 4.—*World production of monazite concentrates by countries* [1]

[Short tons]

Country [1]	1954–58 (average)	1959	1960	1961	1962	1963
North America: United States (shipments)	[2] 1,364	770	[3]	[3]	[3]	[3]
South America: Brazil	828	1,222	1,153	[4] 930	3,858	1,874
Asia:						
Ceylon	90	94	370	239		
India	[5] 4,122	[6]	[6]	[6]	[6]	[6]
Indonesia	[7] 67	[6]	[6]	111	153	[6]
Korea, Republic of [8]	524	65	11	854	[6]	[6]
Malaysia (exports)	481	264	47	780	702	991
Thailand	[9] 28	[6]	[6]	[6]	[6]	
Africa:						
Congo (Leopoldville)	2					
Malagasy Republic	114		471	503	702	[10] 756
Mozambique	[11]		1	[11]	[11]	[6]
Nigeria	51	15	13	8	10	12
South Africa, Republic of	[4] 8,890	2,402			5,326	2,300
United Arab Republic (Egypt)	3	[4] 165	[6]	[6]	[6]	[6]
Oceania: Australia [12]	337	401	405	1,733	912	[4] 2,300

[1] Monazite is also produced in U.S.S.R., but no data are available.
[2] Average annual production 1957–58.
[3] Figure withheld to avoid disclosing individual company confidential data.
[4] Estimate.
[5] Data for the year 1958 only.
[6] Data not available.
[7] Average annual production 1954–55.
[8] Reported as concentrates containing 45–55 percent of rare-earth oxides; also reported as 30 percent cerium, which may be high.
[9] Average annual production 1956–58.
[10] Exports.
[11] Less than 0.5 ton.
[12] The data listed represent the total for high-grade, low-grade, and concentrate.

TABLE 5.—*Exports of thorium products*

Year	Class 6255.0			Class 6257.0	
	Number of countries	Pounds	Value	Pounds	Value
1961	16	102,352	$378,916	260	$16,693
1962	19	1,094,566	357,563	980	46,513
1963	22	40,340	264,235	1,316	50,506

STRATEGIC CONSIDERATIONS

The Office of Emergency Planning established on March 13, 1964, a new stockpile objective of 500,000 pounds for thorium. The inventory of strategic and critical inventories on June 30, 1964, contained 848,354 pounds of residues in the Defense Production Act inventory and 3,965,441 pounds (ThO_2 equivalent) in the Supplemental Barter inventory.

The President may direct AEC to acquire such quantities of special nuclear material as he deems necessary in the interest of national defense. It is known that AEC purchased thorium in the past, but the quantities were not disclosed until 1959. To fulfill the military requirement as well as for their own research program, AEC has an inventory of thorium, just as is the case with the military stockpile of uranium and its byproducts. A summary of AEC activity in thorium is shown in table 6.

Resources of thorium in the United States assure complete self-sufficiency for any conceivable contingency, even though at present these resources cannot be exploited economically. In addition, the large potential resources in the Blind River and other areas of Canada provide assurance of self-sufficiency for the North American Continent. Brazil's large reserves of monazite form a third source of supply within the Western Hemisphere. The sudden large-scale development of thorium breeder reactors would not suffer from lack of resources. Processing facilities are capable of a manyfold increase in demand, and could be expanded quickly.

TABLE 6.—*Thorium activity of AEC, fiscal years 1959–64*

[Thousand pounds]

	1959	1960	1961	1962	1963	1964
Procurement	124.1	96.1	31.7	0.6	0.8	0.7
Consumption	15.4	25.7	132.2	50.6	72.9	135.4
Disposal	4.3		4.8		5.6	.1
Material on hand at end of fiscal year	3,793	3,864	3,758	3,708	3,630	3,496

Source: AEC, Office of the Controller, August 1964.

GOVERNMENT PROGRAMS

Thorium was included in the list of minerals eligible for financial assistance in the national minerals-exploration program of the Defense Minerals Exploration Administration (DMEA) instituted under the Defense Production Act of 1950, as amended. DMEA expired June 30, 1958, and a similar program continued under the Office of Mineral Exploration (OME). A total of nine exploration contracts, solely for thorium, were made in nine States, for $206,244, of which Government participation was $167,158. Thorium often appeared as a secondary commodity in many applications for DMEA aid for uranium and rare-earth mineral prospects. At present, up to 50 percent of the allowable cost of authorized exploration is contributed by the Government.

AEC is charged with the control of all fissionable material and any source material used to produce fissionable materials. More explicitly, source material means any material, except fissionable material, which contains 0.05 percent or more of uranium, thorium, or any combination thereof. Unless authorized by a license isued by AEC, no person may transfer, deliver, or export any source material after removal from its place of deposit in nature. Application for license is available from AEC and, upon determination that an application meets the requirement of the Atomic Energy Acts of 1946 and 1954 and of the regulations of AEC, a license will be issued in the form and upon the conditions deemed appropriate and in accordance with law. The conditions imposed include the filing of reports and restriction upon the use of source material.

As of October 1964, nine States—Arkansas, California, Florida, Kansas, Kentucky, Mississippi, North Carolina, New York, and Texas—have assumed cooperatively some of AEC licensing and other regulatory authority over the uses of radioactive materials within the State. About 20 other States have passed enabling legislation to permit negotiations with AEC. State responsibility is usually vested in the State board of health (or agency or department, as the case may be). Criteria for issuance of licenses will be the same as used by AEC. Provisions are made for exemption of certain quantities and concentrations of radioactive material, and any person may receive, possess, or use products or materials containing radioactive material in amounts or concentrations not in excess of those listed in the published exempt schedule.

In August 1964, the Atomic Energy Act of 1954 was amended to permit private ownership

of nuclear materials. By January 1, 1971, all new distributions of nuclear materials must be by sale, rather than by lease as at present, and by June 30, 1973, all leased material must be purchased by the leasing firm or returned to AEC. AEC will still retain its licensing and regulatory functions.

PRICES AND COSTS

Quoted monazite prices have been relatively stable for several years and have been quoted nominally, depending on the grade, at 13 to 20 cents per pound for material containing 55 to 68 percent total rare-earth oxides, including thoria. Metallurgical-grade thorium oxide (99.8 percent ThO_2) was quoted by Rio Tinto Dow, Ltd., of Canada at U.S. $4.63 per pound and metallurgical-grade thorium fluoride was U.S. $3.93 per pound.

Domestic thorium oxide, ceramic-grade (99 percent), was offered at $7 per pound in lots of 10 to 49 pounds, and the high-density grade (also 99 percent), was $10 per pound. Thorium nitrate, wire-grade, ranged from $2.50 to $3 per pound, and the mantle-grade ranged from $2.65 to $3.15 per pound. Thorium-magnesium master alloy containing 30 to 40 percent Th was quoted at $9.18 to $10 per pound of contained thorium, plus the contained magnesium at $0.3625 per pound. All prices were quoted f.o.b. destination, continental United States, and the range in prices depended on the quantity per shipment.

Thorium metal, reactor grade (99.9+ percent), was $20 per pound, and metal pellets were $15 per pound. The new high-temperature alloy, TD Nickel, containing about 2 percent ThO_2 dispersed in the nickel, was offered at $30 per pound in sheet form and $20 per pound in bars.

TAXES

Depletion allowances for the mining of thorium minerals, under the Internal Revenue Code of 1954, is 23 percent for domestic operations and 15 percent for foreign operations.

RESEARCH

As part of its nuclear research program, AEC has conducted extensive investigations to advance the use of thorium in reactors. Phillips Petroleum Co., AEC principal contractor at the National Reactor Testing Station in Idaho, has conducted reactor physics studies on the irradiation of Th^{232} in the production of U^{233}. This work has given much fundamental data on the production rate of U^{233} under neutron bombardment, as well as the buildup of other nuclides.

AEC began a long-range program in 1959 at the Oak Ridge National Laboratory, Oak Ridge, Tenn., known as the Thorium Utilization Program. Technology related to the use of thorium-based fuel in fluid-fuel, thermal breeder reactors, and much information have been developed on the Th^{232}-U^{233} fuel-cycle. Some of this work has been conducted with the Brookhaven National Laboratory, where a wide range of U^{233}-Th lattices will be studied. A former program on the Liquid Metal Fuel Reactor concept was conducted at Brookhaven. While this particular type of reactor had many disadvantages and work on it was abandoned, it yielded much information on the use of thorium in reactors.

AEC plans a further long-range program at a new installation to be called the Thorium-Uranium Cycle Development Facility. This facility should demonstrate various fuel recycle processes for the several reactor types that operate best on thorium-uranium fuel.

The Sodium Reactor Experiment began operation in 1957 as an experimental nuclear power plant (5,000 kilowatts) to develop technological data. The core was fully enriched uranium-thorium alloy and the coolant was liquid sodium which enters the reactor at 530° F and leaves it at 960°. The hot sodium produces steam at 600 pounds per square inch pressure and 825° F.

AEC is contributing up to $14.5 million for research and development assistance in connection with the Peach Bottom, Pa., reactor. This plant was built primarily as a prototype for a large central power-generating station.

Private and university research has contributed greatly to new knowledge on thorium uses, much of it financed by the Government under contract or as fellowships. The Babcock & Wilcox Co. expects to study the spectral-shift reactor concept at a new major fuels development center at Lynchburg, Va. This reactor appears to be well suited for thorium fuel. Allis-Chalmers Manufacturing Co. has collaborated in the construction and operation of a thorium reprocessing facility in Italy where a fast uranium-thorium reactor, called rapid thorium-uranium-sodium (RAPTUS) has been under development. This facility will reprocess and refabricate fuel from the Elk River reactor.

A review symposium on the thorium fuel cycle was held in December 1963 at Gatlinburg, Tenn., and the 33 papers presented were published in 2 volumes (*1*).

Despite the progress made, breeder reactors have not yet reached an economically useful stage of development, and from 20 to 40 years of intensive research lie ahead. Even when breeders become commercial, they will not make new fissionable material fast enough to provide fuel for new plants at the rate required if

nuclear power is to increase its proportional share of the Nation's electric-power load. Even after successful breeder reactors are developed, it will be necessary to fuel initial installations with U^{235} until sufficient U^{233} can be produced to meet the needs. Fortunately, with thorium breeder reactors, the intermediate needs can be met by substituting U^{235} for U^{233}. Considering that many decades will be necessary before nuclear reactors can displace fossil fuels in the Nation's economy, even after a successful breeder reactor is developed, research should continue at a rapid rate to assure a means of conserving all forms of energy.

The Bureau of Mines has contributed research efforts on the extraction and production of thorium as domestic problems have appeared. Other work has been done on methods for producing high-purity thorium, arc melting of thorium and other melting techniques, and the production of thorium alloys. The Geological Survey has conducted much work on the geology and geochemistry of thorium as aids to the prospector in locating thorium deposits.

OUTLOOK

Thorium production for nonenergy uses will probably increase gradually over the next two decades. This will result from increased use of thorium in magnesium-thorium alloys, the recently developed TD Nickel (nickel strengthened with a dispersion of about 2 percent ThO_2), and thoria refractories. Use in gas mantles, which still consumes large quantities of thorium nitrate, will continue at about the present rate, and some new uses may serve to raise the growth rate above the percentage increase in the gross national product.

Until demand for thorium exceeds supply from the sources now available, domestic requirements will continue to be imported. Canadian thorium, derived as a byproduct from uranium mills, will probably dominate the market, with imported monazite which has been derived as a byproduct of dredging of titanium, tin, and zirconium minerals, running a close second. Domestic thorium will continue to be produced only as a byproduct from placer mining operations such as those for titanium in Florida. Economic utilization of other thorium deposits would require a substantial increase in price. However, should demand warrant this, ample domestic resources are known and could be developed to supply the need.

Energy uses for thorium will continue on an experimental basis over the next decade at about the same rate. Such experiments require years to complete and, barring some sudden discovery, development of a full thorium-breeder reactor will take from 30 to 40 years, about the same length of time estimated for the development of the uranium-breeder reactor. Thorium has gotten a relatively late start in its development as a nuclear fuel, and the outcome in the race between the two is uncertain. In the long distant future when fossil fuels are exhausted, both thorium and uranium will probably find specific applications and complement each other.

The U.S. Atomic Energy Commission (AEC), under its civilian nuclear power program, will continue to cooperate in the research and development of thorium breeder reactors under its thorium utilization program. A thorium-uranium 233 fuel cycle development facility is scheduled for completion in 1966. The spectral shift reactor concept will also be advanced as a joint AEC-industry project, likely first as a uranium breeder and then as a thorium breeder. Several foreign countries are also committed to similar work.

PROBLEMS

Processors who recover thorium from monazite have the problem of equating supply and demand between thorium and the rare-earth metals. Furthermore, their supply of monazite comes from areas widely scattered around the world and is largely a byproduct of the recovery of titanium and zirconium minerals. The supply factor will be more acute than in the past, because the principal world producer of monazite has closed its mine in the Republic of South Africa for an indefinite time. To cope with these problems, processors are required to carry large stocks of raw concentrates, in-process materials, and finished or semifinished products.

Simpler and more economical methods of separating thorium and producing pure products are required. The prices of thorium products are high, discouraging their use in many nonenergy uses, and this fact may even tilt the balance in favor of uranium in nuclear power reactors.

Domestic producers of thorium have not been able to compete with imported materials. Foreign monazite, generally speaking, has been

richer in thorium, and the market has not been sufficiently broad to warrant development of the higher grade thorite deposits found in the western States. Thorium obtained as a by-product from Canadian uranium ores will probably dominate the near-term market at prices that are uneconomic for domestic producers. There is a need to develop low-cost mining and extraction methods for domestic thorium mineral deposits.

Development of thorium for nuclear purposes encompasses broad fields and disciplines as the development of uranium nuclear science and technology. Many of the factors being discovered in uranium reactors will be useful in thorium reactors. There is one difference, however; natural thorium has no fissionable component, and reactors using thorium for fuel will have to be of the breeder type in which excess neutrons convert Th^{232} to U^{233}. So far, thorium reactors have been operated with mixed thorium and enriched uranium, in which U^{235} provides the neutrons for the chain reaction and for breeding U^{233}. A reactor using a thorium-U^{233} cycle has not been operated, as insufficient U^{233} has not yet been produced. Until such a reactor can be operated and sufficient recycling data have been obtained, the future of thorium reactors can only be judged on theoretical aspects.

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TIN

By John E. Shelton [1]

THROUGH use first in bronze and later in pewter, tin-plated iron, and solders, tin shares with a few other metals the distinction of 5,000 years of use by mankind.

Cassiterite, tin oxide, is the only commercial mineral of tin. Although cassiterite deposits are known throughout the world, those of economic importance are limited to a few areas. The principal areas are the placer deposits in Asia and Africa and the lode deposits in South America. There are no known tin deposits of economic grade or size in the United States.

World mine production was 190,300 tons in 1963. Principal contributors were Malaysia 31 percent, China 15, Bolivia 12, U.S.S.R. 10, Thailand 8, Indonesia 7, Nigeria 5, and the Congo (Leopoldville) 3; the remaining 9 percent came from 27 other countries with smaller annual outputs of 5,000 tons or less.

Consumption of tin in the United States in 1963 was 78,000 long tons—55,000 tons of primary and 23,000 tons of secondary. Annual consumption in the 5-year period 1959–63 averaged 79,000 tons—52,000 tons of primary tin and 27,000 tons of secondary tin. The domestic primary-tin supply consisted of imported metal and metal recovered from imported tin concentrates at the Texas City, Tex., tin smelter. Secondary tin was recovered as metal, compounds, and as alloys. In 1963, 14 percent was recovered as metal and 3 percent as compounds, mostly from tinplate scrap. The remainder was recovered in the form of alloys from copper-, lead-, and tin-base scrap.

The principal uses of tin are in the production of tinplate, solder, bronze, brass, and babbitt and in tinning; small quantities are used in metallic forms, miscellaneous alloys, and chemicals.

The short-term outlook is that primary world mine production will be several thousand tons lower than demand. Consumption of tin will rise as the standard of living and industrialization increases throughout the world. World mine production probably will increase at about the same rate as the increase in demand.

The disposal of surplus tin in excess to the U.S. national (strategic) stockpile totaled 12,000 tons by December 31, 1963. The disposal will continue for 5 to 7 years and will help to fill the gap between demand and supply.

In the United States the tin-consuming industry is confronted with problems relating to tin supply and price; the domestic problems are the needs (1) to develop a primary source of tin and (2) to improve secondary sources of tin supply.

BACKGROUND

Tin has been important in commerce since about 3000 B.C. Tin is a constituent of bronze which was known to ancient man. Copper was coated with tin at the beginning of the Christian era and tinplated iron was first manufactured in the 16th century.

Tin always has been an international metal. The Phoenicians were attracted to Cornwall for tin over 20 centuries ago. Production of tin before 1800, unlike that of most base metals, was relatively large compared with that since 1800. Production before 1800 was over 3½ million tons compared to over 10 million since 1800. Modern society has required an increasing quantity of tin. At the beginning of the 19th century, tin was used chiefly in bronze, pewterware, and as a lining for copper cooking utensils. Since 1800, the adoption of the steam engine and power-driven machinery, which required bronze and soft-metal bearings, the development of tin-plated containers for food and other products, electrical power machinery, automobiles, and airplanes have resulted in increased demand for tin. To meet this increase in demand, world mine production has grown to 190,000 long tons in 1963. In world output, tin ranks fifth among the nonferrous metals behind aluminum, copper, lead, and zinc.

[1] Commodity specialist.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Of the total world mine output in 1963, Malaysia produced 31 percent, China 15 percent, Bolivia 12 percent, the U.S.S.R. 10 percent, Thailand 9 percent, Indonesia 7 percent, Nigeria 5 percent, Congo (Leopoldville) 3 percent, and other countries 8 percent.

About 70 percent of the world output of primary tin is smelted in 10 countries: Malaysia 44 percent, United Kingdom 9 percent, Nigeria 5 percent, Belgium 4 percent, Netherlands 3 percent, and Australia, Bolivia, Congo (Leopoldville), United States and West Germany 1 percent each. Total smelter capacity in these countries is over 200,000 tons annually. In addition to the major tin smelters, there are a number of small units treating local output.

Over one-third of the total free world primary and secondary tin production is consumed in the United States. The United Kingdom is the second largest consumer of tin, followed by Japan, West Germany, and France in that order. In the United States, about 280 of a total of 1,800 plants consume 95 percent of the total tin and are chiefly in the Eastern States. Almost one-third of the tin consumed in the United States is derived from secondary materials.

THE INTERNATIONAL TIN AGREEMENT

The First International Tin Agreement was signed or ratified by 20 tin producing and consuming countries and became effective on July 1, 1956. The Second International Tin Agreement came into force on July 1, 1961, having been formally signed or ratified by 6 producing and 14 consuming countries. Three of the larger consuming nations, the United States, U.S.S.R., and West Germany, did not sign or ratify either agreement.

The stated objectives of the agreement are (1) to insure adequate supplies of tin at reasonable prices, and (2) to prevent excessive fluctuations in the price of tin. The governing body is the International Tin Council, composed of a representative from each producing and consuming member government. The producing countries have 1,000 votes distributed, so that each country has 5 initial votes and an additional number corresponding to their proportionate production. The consuming countries also have 1,000 votes, 5 initial votes for each country and an additional number proportionate to their consumption. The voting power may be changed to meet changing conditions.

The First Agreement established a floor price of £640 per long ton (80 cents per pound) and a ceiling price of £880 (110 cents). The floor and ceiling prices have been raised several times and on December 5, 1963, the floor price was raised to £850 per ton (106.25 cents per pound) and the ceiling price was raised to £1,000 (125 cents). The agreement provides for establishing a buffer stock of 25,000 long tons of tin or equivalent in cash. Contributions, not to exceed 75 percent in metal, of metal or cash are compulsory for producing countries. Additional voluntary contributions may be made by producing or consuming countries.

Under the agreement, when the price of tin is at or above the ceiling price, the buffer stock manager must offer tin for sale if he has tin available. When the price is at or below the floor price, the manager must buy tin if he has funds. The range between the floor and the ceiling is divided into three sections. As established on December 5, 1963: In the lower range £850–£900, (106.25–112.50 cents), the manager may buy tin; in the middle range, £900–£950(112.50–118.75cents), he neither buys or sells unless the Council directs otherwise; in the upper range, £950–£1000 (118.75–125.0 cents), he may sell.

The buffer stock manager bought tin in 1958 in an attempt to support the floor price of £730 per ton (91.25 cents per pound) until funds (both regular and special voluntary contributions) were depleted in September. In 1959, the manager liquidated tin acquired by the special fund. The remaining tin was sold in 1961 in an attempt to maintain the ceiling price of £880 per ton (110 cents per pound). The manager entered the market briefly in the fall of 1962 to support the floor price of £790 (98.75 cents) and again in 1963, in an attempt to maintain the ceiling price of £965 (120.625 cents).

Control of exports of tin by member producing countries was in effect from December 15, 1957, to September 30, 1960. The buffer stock manager was permitted to operate in the middle-price range to prevent a sharp rise in the price of tin when the export control first became effective.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Primary or virgin tin is metal produced from ore. It is cast and sold as bars, ingots, pigs, and slabs in weights of 112 pounds or less; most of the tin imported into the United States is 100-pound pigs.

Tin specifications of quality are determined principally by brand names that indicate the smelter and source of the ore. The important classes are Grade A and common tin. Grade A comprises several registered brands which

must assay 99.75 percent tin. One of the best-known brands included in the Grade A class is Straits, a product of Malayan smelters that averages about 99.9 percent tin. Common tin consists of brands assaying 99 to 99.75 percent tin. When the Texas City smelter was owned by the Government, most of the tin produced was Longhorn 3 Star Brand, containing a minimum of 99.8 percent tin.

As the United States has been dependent upon foreign tin producers, domestic industrial tin specifications have not been established. However, to provide a guide for selecting tin for various applications, the American Society for Testing Materials has proposed a tentative classification of pig tin based on market practice, grades of tin in the strategic stockpile, and use.

TABLE 1.—*Classification of pig tin*

Designation		Description		General applications
ASTM	Commercial	Class	Minimum tin content (percent)	
AA	Electrolytic	Extra-high purity.	99.98	Analytical standards, research, pharmaceuticals.
A	Grade A	High purity	99.80	Food containers, foil, collapsible tubes, block tin products.
B		Lower grade	99.7	Less exacting general purposes, electrotinning.
C-1	Common	Copper alloying.	99.0	Cast bronze, bearing metal.
C-2	do	Lead alloying	99.0	Solders, lead-base alloys.

Secondary tin metal, recovered mostly from tinplate scrap, has a purity of about 99.98 percent. M&T and Vulcan are representative brands of this class of tin.

TECHNOLOGY

Geology

The only mineral of commercial importance as a source of tin is cassiterite (SnO_2), although small quantities of tin are recovered from the complex sulfides—stannite, cylindrite, and teallite. Cassiterite has a high specific gravity (6.8 to 7.1), a hardness of 6 to 7, and usually a dark brown or black color and an adamantine luster.

The main sources of tin are placer and eluvial deposits, derived from weathering and erosion of vein and disseminated replacement tin deposits. In the placer deposits the cassiterite is relatively free of impurities because it had greater resistance to weathering than minerals originally associated with it.

Primary tin deposits are associated with granite, granodiorite, quartz monzonite, and related porphyries and pegmatites. In contrast to placer deposits, primary tin deposits usually have other minerals, mostly sulfides, containing antimony, arsenic, bismuth, columbium, copper, iron, lead, silver, tantalum, tungsten, or zinc, in the veins with the cassiterite.

Mining

The principal method of mining placer tin deposits is bucket-line dredging, although gravel-pump, hydraulicking, and various open-pit methods also are used.

Bucket-line dredges, similar to floating dredges used to mine other placer deposits, are used. The ore is excavated and transported by buckets to the interior of the dredges, washed on screens, and concentrated on jigs and shaking tables. Tailings are discharged at the rear of the dredges to fill in the mined pond, and the rougher tin concentrate is sent to the dressing sheds for final concentration. Dredges to mine the offshore tin deposits of Indonesia at depths up to 150 feet below the ocean surface are being developed.

Gravel-pump and hydraulic mining are similar in that both mining methods use water jets to break up the tin-bearing material. The methods of conveying the material to the launders differ. In gravel-pump mining a pump is used, whereas in hydraulicking the pressure developed by a natural head of water is employed. In each method the material is washed through a riffled launder, called a palong in Malaysia, where the cassiterite is collected by the riffles and the waste is washed free.

In other open-pit operations the material is excavated dry by power shovels and transported on a conveyor belt to the washing plant for treatment.

A small quantity of tin is mined in Malaysia by dulang washers—one of the oldest methods of mining tin ore and traditionally limited to women workers. A dulang is a round wooden tray somewhat like a gold pan and is worked by hand.

Vein tin deposits are mined by methods similar to those used in the hard-rock mining of other nonferrous ores. Access to the ore bodies is by adits and shafts, the ore is broken by conventional drilling and blasting, and the ore is transported from the mine to a concentrator for treatment.

Beneficiation

Impure cassiterite concentrate from dredges, launders, and other mining of placer deposits is upgraded by washing, tabling, and magnetic or electrostatic separation. Final cleaning is

done by hand washing—a method used for hundreds of years. Virtually the entire product is cassiterite containing more than 75 percent tin.

Tin ore from lode deposits is reduced to the necessary size by conventional crushing and grinding. The ore is concentrated by gravity methods, involving screening, classification, jigging, and tabling. The concentrate is usually a lower grade (60–70 percent tin) than placer concentrate owing to associated sulfide minerals. The sulfide minerals are removed by flotation or magnetic separation with or without magnetic roasting.

Recovery of tin is low, ranging from 50 to 80 percent, in the concentration of both placer and vein cassiterite ore because the finely divided cassiterite is difficult to recover. Successful flotation of tin ores has never been achieved, although considerable flotation research has been done.

Smelting

Cassiterite is reduced to tin by heating with carbon at 1,200° to 1,300° C. The tin concentrate from alluvial deposits is almost pure cassiterite and is smelted directly. Other concentrates, particularly from vein deposits in Bolivia, contain impurities that must be removed before smelting. This is usually done by roasting the tin concentrate with or without fluxes, followed by water or acid leaching. During roasting, most of the sulfur and arsenic are removed as oxides; bismuth, copper, iron, and zinc sulfides are converted to oxides, and lead sulfide is oxidized to the sulfate. Bismuth, copper, iron, and zinc oxides are removed by leaching the roasted concentrate with dilute hydrochloric acid. Tungsten may be recovered by roasting the concentrate with sodium carbonate or sulfate and leaching with water. Antimony, bismuth, lead, and silver, may be removed by a chloridizing roast followed by an acid leach.

In modern tin-smelting plants, reverberatory furnaces are used to smelt primary-tin concentrate and to resmelt the slag for additional tin recovery. Although blast and electric furnaces also are used to smelt tin concentrate, reverberatories are preferred because of better control, cleaner slags, and superior efficiency in smelting finely divided material.

Tin smelting is a batch operation. A typical charge consists of cassiterite, a carbon reducing agent, and limestone and silica fluxes. From 10 to 12 hours is required to smelt a charge. When smelting is complete, the molten batch is tapped into a settler, from which the slag overflows into cast-iron pots. The molten tin from the bottom of the settler is cast into slabs or pigs (of about 75 pounds) for refining.

After cooling and solidifying, the slag, containing 10 to 25 percent tin, is crushed to minus ¾ inch for resmelting. The reduction of tin silicate in the slag is more difficult than the reduction of tin oxide in the ore, and a higher temperature (up to 1,480° C) is necessary. Anthracite is used as a reducing agent, limestone as a flux, and either iron or lime to aid in the reduction and to replace tin in the silicate. Slag from the resmelting contains less than 1 percent tin.

Refining

Most tin produced in smelting concentrate and slag contains various metallic impurities that were reduced with the tin and must be removed before the tin is marketed. Refining may be done by heat treatment or electrolytic processes. Heat treatment is the most widely used method and may consist of one or both of two operations: (1) Liquating or sweating and (2) boiling or tossing.

In liquating, always the first operation in the sequence, the tin is heated on an inclined hearth to a temperature slightly above the melting point of pure tin but below the melting points of the impurities. Thus, the comparatively pure tin melts and flows into a kettle, leaving impurities such as iron and copper in a dross residue that is re-treated to recover the contained tin.

The molten tin is then poled with green wood, which produces a strong boiling action. During poling, the metal impurities and part of the tin are oxidized and form an oxide dross that is skimmed off. Sometimes tossing is used instead of poling. In this operation hand ladles of molten tin are dipped from and poured back into the kettle, exposing the tin to the oxidizing action of the air. Boiling or tossing is continued until the desired grade of refined tin is obtained. After refining has been completed, the tin is cast into pigs for marketing.

Electrolytic refining of tin has been used successfully to produce a purer product than heat treatment. However, owing to a low demand for extremely high-purity tin, the more costly electrolytic process seldom has been used to refine primary tin.

USES

Tin, symbol Sn, is a silvery white metal with a specific gravity of 7.29. It melts at 231.9° C, boils at 2,270° C, and changes to another form, gray tin, at 13.2° C. An unusual combination of properties—low fusibility, malleability, resistance to corrosion and fatigue, and ability to alloy with other metals—accounts for the many uses in which tin is preferred to other competing materials.

The largest use of tin is as a protective coating for copper, steel, and other stronger materials, mainly in the form of tinplate for cans. Tinplate is thin, sheet steel coated with commercially pure tin by hot-dip or electrolytic processes. Another older but minor use of tin as a coating is in the production of terneplate—sheet steel covered with a tin-lead alloy. Tin is also used as a coating on copper wire and electrical connections to prevent corrosion by the insulation and to facilitate soldering.

The second largest use of tin is in soft solders—tin-lead alloys. Because tin alloys readily with most metals, it is the essential constituent of the solders. However, the addition of lead not only reduces the melting point and cost of the solder but also increases its strength.

One of the first-known and currently larger uses of tin is in making bronze and brass. The principal tin bronzes are the phosphor bronzes (up to 12 percent tin), which have high strength, excellent resistance to corrosion, and superior bearing characteristics, and the gun metals (8 to 10 percent tin), which are used for gas-free, pressure-tight, and corrosion-resistant castings.

Substantial quantities of tin are used in producing babbitt, pewter, type metal, and die-casting and in fusible alloys. Although the use of tin in pipe, tubing, collapsible tubes, and foil has declined, tin is still preferred in applications that require purity and nontoxicity. Small quantities of tin are consumed in chemical reagents and compounds used in making glass, ceramics, and other products. Recently developed organotin compounds, containing 25 to 50 percent tin, are used as stabilizers in plastics, wood preservatives, fungicides, insecticides, and similar uses.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Columbium, tantalum, and tungsten are the principal byproducts of tin placer and vein deposits. Tin is recovered as a byproduct of molybdenum at the Climax mine in Colorado and of lead-zinc at the Sullivan mine in British Columbia, Canada, but this output is a negligible part of world production.

ALTERNATE MATERIALS

In the largest use of tin—tinplate for cans—there are numerous alternate materials, including glass, paper, enameled steel, plastics, and aluminum. Nonmetallic materials, and copper, aluminum, and zinc-coated products have largely replaced tinplate and terneplate for roofing and construction.

In solder, silver or antimony may be used in place of tin. In other alloys, low-tin bronze and roller or ball bearings may be substituted for babbitt metal containing tin.

Wrapping material, such as aluminum, plastics, or paper, may be used instead of tinfoil. Other chemical compounds may replace tin compounds for use as fungicides and insecticides, slime-control reagents, and an enamel opacifier in ceramics.

SECONDARY SOURCES AND RECOVERY

About 80 percent of the tin reclaimed each year from secondary materials is derived from copper- and lead-base alloys and 20 percent from tinplate and tin-base alloys. Of the total secondary tin recovered in 1963, over 80 percent was recovered as a component of bronze and brass, solder, type metal, babbitt, and miscellaneous tin-lead alloys in about 160 plants, principally in the Eastern United States. About 14 percent was recovered as metal and 3 percent as chemicals, mostly at 12 detinning plants scattered throughout the United States. Although small quantities of tin are also recovered at detinning plants from used tin containers, such reclamation has been attractive only under emergency conditions, owing to the high cost of collecting, transporting, and cleaning the cans.

Of the 5,361,000 short tons of tinplate produced in 1963, only 673,000 tons of waste plate was treated for reclamation of the contained tin, and the tin reclaimed from waste plate represented only about 10 percent (2,900 long tons) of the tin used in tinplate production (28,000 tons).

Several methods of recovering tin from tinplate scrap have been proposed, but three have accounted for nearly all commercial detinning—the alkali-chemical, the alkaline-electrolytic, and the chlorine processes.

In the alkali-chemical process (most widely used), the tinplate scrap is treated with a hot solution of caustic soda in the presence of an oxidizing agent. The tin is dissolved as sodium stannate and leaves the steel, which is washed and pressed into bales for shipment. The tin may be recovered from the stannate solution as metal, as sodium stannate crystals, or as tin oxide. Because of advantages in processing costs and production of a high purity metal, the common practice is electrolysis of the solution to yield metallic tin. The refined tin averages as high as 99.99 percent pure, with antimony, iron, and lead as principal impurities.

RESERVES

The free world reserves of tin are estimated to total 4.7 million long tons of contained tin. Of this total, 3 million tons is in Burma, Indonesia, Malaysia, and Thailand, 0.75 million

tons in the Republic of the Congo and Nigeria, 0.75 million tons in Bolivia and 0.20 million tons in the rest of the free world. These figures do not include the potential resources in the offshore deposits of Indonesia and Thailand. The Rondonia Province, Brazil, reportedly may have very large tin resources.

The tin reserve in the United States, mostly at Lost River, Alaska, is estimated by the Geological Survey and the Bureau of Mines at about 3,000 tons. Estimated reserves in Canada are 30,000 to 40,000 tons.

Reserves in the U.S.S.R. are estimated at about 0.5 million tons.

CONSERVATION PRACTICES IN PRODUCTION AND USES

The principal and most effective method of conserving tin is the electrolytic process of tin plating. In World War II, when the domestic tin supply was restricted, an electrolytic process was adopted. Since then, this method has progressively replaced the hot-dip method of tinplating. Coatings of any thickness, but usually ranging from 15 to 45 millionths of an inch, can be applied with electrolytic methods, whereas the minimum coating possible with hot-dip methods is 70 millionths of an inch. Moreover, in electroplating, a different thickness of tin can be applied on each side of the same sheet, thus reducing tin consumption.

After the first large-scale use of electrolytic tinplating in 1943, its share of the annual domestic tinplate output rose from 16 to 96 percent in 1963. Despite an increase of 141 percent in annual tinplate output during that period, annual consumption of tin for tinplate increased only 34 percent, as the quantity of tin used per short ton of plate dropped from 23.4 to 12.9 pounds. In 1960 double-reduced tinplate was introduced. After a second reduction, the thickness is one-half to two-thirds that of normal tinplate, resulting in more tinplate area for a given weight of steel. The weight of tin is about one-half that normally contained in tinplate.

Other conservation measures adopted during periods of limited tin supply include the use of aluminum, lead, and tin-coated lead to replace tin in collapsible tubes.

SOURCES OF STATISTICAL INFORMATION

Monthly and annual data on domestic production, distribution, stocks, receipts, shipments, and uses of primary and secondary tin are obtained by the Bureau of Mines. World production data on tin also are compiled by the Bureau from State Department dispatches, and official publications of foreign countries, and U.S. imports and exports of tin are obtained by the Bureau of the Census. The International Tin Council publishes detailed monthly data on primary production, consumption, stocks, trade, uses, and other phases of the tin industry throughout the world. As a result, nonfinancial statistical data on the world tin industry are comprehensive and relatively adequate except for data on secondary tin production.

TABLE 2.—*World mine production of tin (content of ore), by countries*

[Long tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963
Bolivia (export)	25,823	23,811	19,407	20,409	21,492	22,752
Congo (Leopoldville)	12,240	9,194	8,636	6,314	6,875	6,488
China	18,700	26,000	28,000	30,000	28,000	28,000
Indonesia	30,041	21,613	22,596	18,574	17,310	12,947
Malaysia	56,396	37,525	51,979	56,028	58,603	59,947
Nigeria	8,177	5,541	7,675	7,779	8,210	8,723
Thailand	10,905	9,684	12,080	13,270	14,679	15,587
U.S.S.R.	11,700	15,000	16,000	17,000	17,000	20,000
Other countries	13,918	13,132	14,027	14,726	14,831	15,856
Total	187,900	161,500	180,400	184,100	187,000	190,300

TABLE 3.—*Secondary tin recovered in the United States*

[Long tons]

Year	In alloys	As metal	In chemicals	Total
1954–58 (average)	22,346	3,222	640	26,208
1959	19,625	3,220	855	23,700
1960	18,130	3,015	905	22,050
1961	17,670	3,000	1,020	21,690
1962	17,195	2,977	868	21,040
1963	18,554	3,061	717	22,332

PRODUCTION, CONSUMPTION, AND TRADE

Production, consumption, and import data are shown in tables. Exports of tin from the United States are small, averaging 1,000 tons annually from 1959 through 1963.

The significant features of these data are the concentration of tin production in the so-called underdeveloped countries, dependence of the domestic primary tin supply of imported

TABLE 4.—*Consumption of primary tin in the United States, by finished products*

[Long tons, tin content]

Product	1954–58 (average)	1959	1960	1961	1962	1963
Alloys (miscellaneous)	345	309	260	300	322	290
Babbitt	2,388	2,157	1,841	1,744	2,186	2,225
Bar tin	1,101	1,174	894	1,165	1,439	1,580
Bronze and brass	3,941	3,868	3,350	3,168	3,959	4,128
Chemicals including tin oxide	631	790	648	674	824	1,088
Collapsible tubes and foil	830	930	788	939	1,010	992
Pipe and tubing	103	79	35	31	30	28
Solder	9,664	7,046	6,660	7,598	12,349	12,856
Terne metal	167	58	132	51	166	298
Tinning	2,304	2,057	1,996	2,035	2,180	2,142
Tinplate	32,504	25,275	33,238	31,185	28,708	28,351
Type metal	129	129	98	96	104	116
White metal	1,183	1,764	1,452	1,190	1,215	1,044
Other	140	197	138	112	110	71
Total	55,430	45,833	51,530	50,288	54,602	55,209

TABLE 5.—*Consumption of secondary tin in the United States, by finished products*

[Long tons, tin content]

Product	1954–58 (average)	1959	1960	1961	1962	1963
Alloys (miscellaneous)	167	138	141	120	106	144
Babbitt	1,890	1,981	1,780	1,794	1,477	1,439
Bar tin	143	243	216	108	110	88
Bronze and brass	13,492	13,241	11,986	13,025	12,428	11,784
Chemicals including tin oxide	932	1,043	1,284	1,415	1,486	1,350
Collapsible tubes and foil	75	113	127	59	79	72
Pipe and tubing	47	40	43	28	14	33
Solder	9,822	12,986	11,618	10,436	7,220	6,739
Terne metal	191	242	337	167	182	263
Tinning	63	74	39	41	59	55
Type metal	1,340	1,263	1,333	1,193	1,212	986
White metal	109	142	90	124	85	95
Other	57	34	36	41	25	46
Total	28,328	31,540	29,030	28,551	24,483	23,094

TABLE 6.—*Tin imported for consumption in the United States, by countries*

[Long tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963
Belgium-Luxembourg	5,316	705	1,601	680	1,826	383
Bolivia	139	325	939	1,672	1,850	1,867
Congo (Leopoldville) and Ruanda Urundi	334	850	336	4		103
Indonesia	187	200	550	150	50	1,023
Malaysia	38,994	22,404	29,521	32,955	34,808	36,410
Netherlands	7,778	2,820	432	55	(1)	25
Nigeria				544	1,176	2,066
United Kingdom	4,894	15,693	5,924	2,810	1,346	1,590
Other countries	420	581	235	1,023	345	134
Total	58,062	43,578	39,538	39,893	41,401	43,601

[1] Less than 1 ton.

TABLE 7.—*Tin concentrate (tin content) imported for consumption in the United States, by countries*

[Long tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963 (tin content) January–August	1963 (gross weight) September–December
Bolivia	6,193	106	117	262	930	790	2,130
Congo (Leopoldville)	512						
Indonesia	4,570	7,946	12,509	8,556	4,321		
Thailand	1,330	2,615	1,336	12		3	
Other countries	290	106	64	87	113		10
Total	12,895	10,773	14,026	8,917	5,364	793	2,140

metal and concentrate, and concentration of more than 90 percent of the domestic tin consumption in five items—tinplate, solder, bronze and brass, babbitt, and tinning. There has been no import duty on tin since 1895. According to the Tariff Schedules of the United States as of August 31, 1963, there was no duty on cassiterite, black oxide of tin, or bars, blocks, pigs, and grain or granulated tin.

Forms of tin that are dutiable include tinplate, pewter, terneplate, foil, powder, chemicals, bottle caps, collapsible tubes, and other manufactured tin items.

STRATEGIC CONSIDERATIONS

The United States is dependent upon foreign sources for supplies of primary tin. Although some tin is mined in the United States, the total production is insignificant. The annual domestic requirements for primary tin are met by imports of metal, metal produced at Texas City smelter from imported concentrates, and release of surplus tin from the national stockpile. Although the recovery of tin from secondary sources in the United States is important, it represents only about 30 percent of the domestic tin consumption.

Because the availability of foreign tin is restricted during wartime, tin has been designated a strategic material for stockpiling. On June 30, 1964, stocks of pig tin totaled 321,600 long tons, of which 314,100 was in the national (strategic) stockpile, and 7,500 in the supplemental stockpile.

GOVERNMENT PROGRAMS

The Office of Minerals Exploration (OME) is authorized to grant loans up to 50 percent of approved costs on exploration projects for tin. No loans have been made by OME.

Tin was removed from the list of materials eligible to be acquired for the supplemental stockpile through barter or exchange transactions on May 18, 1961. During the 1958–61 period, a total of 7,505 tons of tin had been added to the supplemental stockpile.

In 1961 and early 1962, the General Services Administration sold 3,933 tons of tin that was excess to the Government's needs and not in the national stockpile. The disposal of approximately 50,000 tons of pig tin in excess of national stockpile needs was authorized by Congress, June 21, 1962 (H. Con. Res. 473), and sales began September 12, 1962. GSA sold 1,400 tons to industry in 1962, and 9,325 tons to industry, 1,298 tons to the Agency for International Development, and 3 tons to other Government agencies in 1963.

The United States has participated with the International Tin Council in a long-term study of world production, consumption, and reserves and has supplied statistical data for other studies.

During periods of emergency, tin was placed under Government control as to use and allocation. Exports of tin metal and materials containing tin required an export license to all destinations except Canada. In 1953 all controls were removed, except export controls which were extended to June 30, 1965. Exports were under general license to the free world. Entry of Chinese tin is prohibited and a permit is required for U.S.S.R. tin, as it might be of Chinese origin. Entrance of alloys that might include Chinese or Soviet tin also is prohibited.

The United States Tin Corp. Lost River tin mine, Seward Peninsula, Alaska, was granted a Defense Materials Procurement Agency (DMPA) purchase contract in 1951. By October 1954 the corporation had received $2,894,573 to purchase and operate the mine and plant. In 1957, to satisfy a judgment in favor of the Government, the property was offered for sale by bid. No acceptable offer was made and the Government took possession of the property. The property was offered for sale by GSA on August 8, 1960, and sold to Lenhart J. Grother, Red Devil, Alaska, for $21,777.

PRICES

The principal quotations for tin are those at New York, London, and Singapore. Both the Commodity Exchange, Inc., New York, and the London Metal Exchange permit trading in tin for immediate and future delivery.

The price of prompt tin in New York was relatively stable in 1959 and 1960, ranging from 98.0 cents to 104.875 cents per pound. Prices began a general upward trend early in 1961 and rose to 133 cents per pound on December 31, 1963. The average price for 1963 was 116.64 cents per pound, the highest annual average since 1951. Cash tin in London reached £1035.0 per long ton (129.375 cents per pound) in December 1963 and the yearly average was £909.7 per ton (113.72 cents per pound).

In 1961 the price of cash tin in London rose above the ceiling of £880 set by the International Tin Council, reaching £993, when the buffer stock supplies of tin metal were exhausted. When the price dropped below £850 in mid-1962, the "may buy" range at that time, the ITC buffer stock manager bought tin to prevent a further decline. The price began a steady rise and in 1963 the buffer stock was exhausted in an attempt to hold the price at £880.

TAXES

There are no special taxes imposed on the domestic tin industry. Producers are granted

a depletion allowance of 23 percent on domestic production and 15 percent on foreign production.

TRANSPORTATION

Movement of tin concentrate from the mine to the smelter and tin metal from the smelter to the market involves both water and land transportation. Tin is not mined in substantial quantities in the important industrial countries, although some have tin-smelting plants.

Most tin imported into the United States enters North Atlantic ports from the Far East through the Suez Canal and the Mediterranean. Bolivian tin concentrate for the Texas City smelter was transported from the west coast of South America to the Gulf of Mexico through the Panama Canal. Shipments of tin metal or concentrate to the United States take about 2 months from the Far East and about 2 weeks from the west coast of South America.

RESEARCH

The principal tin research organization is the Tin Research Institute, Greenford, England, which is financed by tin producers and controlled by the International Tin Research Council. The research of the Institute is aimed at developing the use of tin through scientific study of the metal, its alloys and compounds, and processes that use tin or may provide future markets. Other research on tin by the domestic consuming industry is concerned principally with improving processes using tin, chiefly tin plating.

The Bureau of Mines and Geological Survey have conducted extensive surveys of domestic tin resources. From 1939 to 1945, as part of the strategic minerals investigation instituted in World War II, special attention was given to tin. All domestic deposits that were believed to have even a remote chance of containing strategic reserves were examined. The information resulting from these investigations indicated that the tin content of domestic deposits was insignificant in terms of national requirements.

The Bureau of Mines conducts research on extracting tin from ores and secondary and waste materials. Through Bureau studies, methods have been developed for recovering tin from ores by chloridization and sulfidization, tin and tungsten from tin smelter slags, tin from hardhead, and lead-tin alloys from solder dross skimmings. In addition, the Bureau continues to examine and evaluate domestic occurrences of tin.

OUTLOOK

The short-term outlook for tin is that primary world production will be several thousand tons lower than demand. Consumption of tin will rise as the standard of living and industrialization in many countries of the world increases. The rising standard of living in these countries results in an increasing demand for tinplate and solder for canning to preserve foodstuff. As countries become more industrialized, the requirements for bronze, brass, babbitt metal, and solder for other than canning becomes greater. Usage of tin in the United States will increase, but the growth rate will be lower than the rise of gross national product in this country and at a slower rate than in many other countries.

World mine production of tin will increase in the near future, but the increase probably will be at about the same rate as the increase in demand. Bolivia, the Congo (Leopoldville), Indonesia, Malaysia, and Thailand, the major tin-producing countries, have the potential to increase production to meet demand, but political and economic upheavals in some of these areas may inhibit realization of this potential and may further enhance the shortage. The world capacity to smelt tin ore is adequate and will become greater since new smelters will be erected in several countries.

Domestic mine production of tin is insignificant and the United States must rely on foreign sources of supply. Part of the U.S. requirements and the world shortage will be met by releases of surplus tin from the U.S. national stockpile. The current disposal program will continue for the next 5 to 7 years by which time increased world mine production may fulfill the needs of the consuming industry.

The search for alternate materials seems likely to be intensified. Plastics, glass, and aluminum will replace tinplate as containers, not so much in present uses, but more in expanding and newer uses. Plastics, aluminum, and chromium coatings on steel may to some extent replace tin as the coating material.

Research is expected to be continued by the Government, industry, and various research institutions to improve extractive processes, improve efficiency and conservation in present usage, and develop new and better uses.

PROBLEMS

The major problem facing the tin industry at this time is the shortage of newly mined tin. This imbalance between supply and demand causes instability in the price which leads the consumer industry to search for alternate materials which may eventually cause the problem of loss of markets by the producers. The loss of markets may affect economic and political disturbances in the countries that depend upon tin mining as a major source of revenue, thus further impeding supply.

There is a pressing need to improve the efficiency of concentration and recovery of the tin mineral cassiterite and improve smelting practices. The depletion of higher grade deposits throughout the world intensifies these problems. Losses of fine tin minerals during concentration and tin in smelter slimes and residues results in a lower efficiency of utilization of resources and increased cost. Production of tin at an acceptable price is necessary to minimize the encroachment of substitute materials and changes in use patterns.

U.S. consumers need more stable supplies of tin. The major potential domestic source is in Alaska, but the remote nature of the deposits and short exploration seasons make evaluation difficult and expensive. Since the Uuited States is dependent upon foreign sources, reducing the loss of tin during use and for improving recovery from secondary sources are problems that need study.

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TITANIUM

By John W. Stamper [1]

TITANIUM is estimated as the ninth most abundant element in the earth's crust and the fourth most abundant of the structural metals. Its oxide has been a commodity of commerce for half a century, but utilization of titanium as a structural metal was made possible only through the advances in technology that followed World War II.

Deposits of the titanium ore minerals, rutile and ilmenite, are widely scattered with major economic deposits found in Australia, Canada, Finland, India, Norway, Malaya, Sierra Leone, Republic of South Africa, and the United States. Virtually all of the rutile mined in 1963 came from sand deposits that were mined by dredging; ilmenite came from rock deposits mined by open-pit methods and from sand deposits that were dredged.

Ilmenite is more abundant than rutile and has traditionally been the principal titanium mineral produced. World output of 2.2 million tons in 1963 was 10 times the quantity of rutile produced. However, rutile contains more titanium than ilmenite and commands a higher price. Various economic and technical considerations necessitate its use instead of ilmenite for some applications.

The chief use of ilmenite is in making titanium dioxide, a white pigment. In recent years, rutile was used principally in welding-rod coatings and for making titanium metal. A commercial process developed in 1958 for making titanium pigment from rutile is likely to make pigment the chief market for rutile as well as ilmenite.

The United States is the principal consumer of titanium minerals and leads in production of ilmenite and titanium metal and pigments. It is largely self-sufficient in ilmenite but imports about 80 percent of its rutile requirements from Australia, the foremost producing country.

Most titanium pigments are made by dissolving ilmenite or titanium slag in sulfuric acid, crystallizing and separating the included iron, then hydrolyzing the solution and calcining the resulting precipitate to pure white titanium dioxide. Pigment plants in the United States built since 1958 utilize the chloride process whereby titanium tetrachloride is oxidized to titanium dioxide—the chlorine being regenerated and used for chlorinating a titaniferous material.

Titanium metal is produced commercially by a process originally conceived by Wilhelm Kroll and developed to industrial scale by the Bureau of Mines. In this process, a titanium mineral, normally rutile, is chlorinated to produce titanium tetrachloride which is then purified and reduced to titanium metal with magnesium or sodium under an inert atmosphere.

During the next decade all segments of the titanium industry should continue to expand. Consumption of titanium dioxide pigment, which on a TiO_2 basis accounts for 95 percent of all uses of titanium minerals, is likely to increase at a slightly greater rate than the Nation's average growth rate. Developments in manned space flight programs, supersonic flight, and deep-diving submarines, foreshadow an ever increasing role for titanium metal. By 1970 annual domestic requirements for titanium minerals may reach 225,000 tons of rutile and 1.3 million tons of ilmenite, including slag.

BACKGROUND

Although the element titanium was discovered by William Gregor in 1790, over 100 years passed before it was put to commercial use. The first commercial application of titanium was as an alloy additive to iron and steel, and the first ferroalloys were produced domestically in 1906. Titanium dioxide pigment was developed later and has been produced in the United

[1] Commodity specialist.

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States since 1918. The use of titaniferous materials in welding-rod coatings first gained acceptance in the mid-1930's and the metal titanium has been of commercial importance only since 1948.

Manufactured titanium dioxide has found an expanding market in the production of paints, paper, and many other products requiring a white pigment with a high hiding power and chemical stability. Based on the TiO_2 content of minerals consumed in production, the output of titanium pigment in 1963 far exceeded the combined production of the other white pigments, white lead, leaded zinc oxide, and lithopone.

The ability of certain titanium compounds to stabilize the electric arc has been known since the 1920's, and the use of these compounds in the manufacture of fluxes and coatings for improved welding-rod has become practically universal.

Because of the importance of titanium metal for defense uses and the complex nature of the new technology involved in its manufacture, the industry received virtually all forms of government assistance during its early expansion. Selecting the Kroll process as the most likely for engineering to industrial scale, the Bureau of Mines developed a practical way to produce the metal in volume in the early 1940's, and commercial production was started by E. I. du Pont de Nemours & Co., Inc., in 1948. Expansion of the industry was phenomenal from 1948 to 1957. However, in 1957, cutbacks in requirement for titanium resulting from changes in military concepts, caused a severe decline in output, and in 1958 the industry operated at only one-fourth of its capacity. Production of the sponge metal doubled during 1959–63.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

The titanium industry is characterized by a moderately high degree of integration from raw materials to semifinished products. Several companies mine and utilize the ore minerals in producing titanium pigments and metal. Significant quantities of titanium materials also are used in the welding-rod, ferroalloy, ceramic, and fiberglass industries.

Minerals

At the end of 1963, seven companies were engaged in mining and concentrating ilmenite and rutile. Operations were in Florida, New York, New Jersey, and Virginia.

The following companies mined ilmenite in 1963: American Cyanamid Co., Piney River, Va.; E. I. du Pont de Nemours & Co., Inc.; Trailridge and Highland, Fla.; The Glidden Company, Lakehurst, N.J.; and National Lead Co., Tahawus, N.Y. Production of both ilmenite and rutile was reported from the following companies: M&T Chemicals, Inc., Beaver Dam, Va.; Florida Minerals Co., Vero, Fla.; and Titanium Alloy Manufacturing Div. of National Lead Co., Skinner, Fla. The Rutile Mining Co. of Florida, produced rutile from a mine near Jacksonville.

A number of localities have produced titanium minerals in the past. The American Rutile Co., a subsidiary of Metal and Thermit Corp., mined a rutile and ilmenite deposit at Roseland, Va., from 1902 to 1949. Between 1932 and 1944 rutile, brookite, and ilmenite were shipped from a rock deposit at Magnet Cove, Ark., owned by the Magnet Cove Rutile Co. The Yadkin Mica & Ilmenite Co., a subsidiary of The Glidden Co., produced ilmenite from a rock deposit at Richland Cove, N.C., from 1942 to 1952. From 1951 to 1955 ilmenite was a by-product of monazite dredging operations in Idaho. Baumhoff-Marshall, Inc., and J. R. Simplot Co. concentrated the heavy minerals at a plant in Boise, Idaho, from nearby deposits worked by Baumhoff-Marshall's dredge and that of the Idaho Canadian Dredging Co. Marine Minerals Division of Heavy Minerals Co., operated an ilmenite and rutile mine at Bath, S.C., from 1956 to 1957.

Another operation on the North American continent is that of the Quebec Iron and Titanium Corp. (Q.I.T.) in Canada. This company is two-thirds owned by Kennecott Copper Corp. and one-third by The New Jersey Zinc Co., a titanium pigment producer. Q.I.T. mines an ilmenite-hematite ore at Allard Lake, Quebec, and smelts this material at Sorel, Quebec, to produce a high titania slag used for making titanium pigment by the sulfate process, and pig iron.

Titanium Pigments

In 1963, the titanium pigment industry was comprised of 5 companies with 10 plants and was concentrated in the eastern part of the United States. Titanium pigments were produced by the following:

Company	*Plant location*
American Cyanamid Co.	Piney River, Va.; Savannah, Ga.
E. I. du Pont de Nemours & Co., Inc.	Edge Moor, Del. (2); New Johnsonville, Tenn; Baltimore, Md.
National Lead Co.	St. Louis, Mo.; Sayreville, N.J.
The New Jersey Zinc Co.	Gloucester City, N.J.
The Glidden Co.	Baltimore, Md.

National Lead and Du Pont were the two largest producers of titanium pigments in 1963. Du pont was the first company to develop the chloride process on a commercial scale and used the method at New Johnsonville, Tenn., and at one of two plants that it operated at Edge Moor, Del. All of the other commercial plants were using the sulfate process.

Cabot Titania Corp., two-thirds owned by Cabot Corp. and one-third by Ruberoid Co., was the latest entrant into the titanium pigment industry, and in 1963 completed construction of a 20,000-ton-per-year plant at Ashtabula, Ohio. The chloride process will be used. Du Pont was building a 27,000 ton-per-year plant at Antioch, Calif., also using the chloride process. Both of these plants were expected to be producing by 1964.

American Potash & Chemical Corp., another new entrant into the titanium pigment industry, was building a 25,000-ton-per-year chloride plant at Hamilton, Miss. In addition, National Lead Company, Pittsburgh Plate Glass Co. and American Cyanamid Co. had plans to construct titanium pigment plants in the United States using the chloride process.

Titanium Metal

At the end of 1963 the following companies were producing titanium sponge metal at the specified locations:

E. I. du Pont de Nemours & Co., Inc., Newport, Del.
U.S. Industrial Chemicals Co. (Reactive Metals Products), Ashtabula, Ohio
Titanium Metals Corp. of America, Henderson, Nev.

Titanium Metals Corporation of America (TMCA) is owned jointly by the National Lead Co. and Allegheny Ludlum Steel Corp. U.S. Industrial Chemicals Co., a subsidiary of National Distillers and Chemical Corp., operated the Ashtabula, Ohio reduction plant.

Du Pont announced it would close its titanium sponge plant early in 1964, owing to available sponge production capacity by integrated producers and increased use of sponge from Japan.

Du Pont and TMCA made titanium tetrachloride for their own use, but U.S. Industrial Chemicals purchased its titanium tetrachloride from Cabot Titania Corp.

The Crane Co., through its subsidiary, Cramet, Inc., produced titanium sponge metal under a Government contract at Chattanooga, Tenn., from 1954 until the early part of 1958 when, owing to lack of a commercial market for its metal, the company closed the facilities. The Cramet plant was turned over to the Government under the contractual agreement and was later dismantled and sold. Dow Chemical Company closed a titanium sponge metal plant at Midland, Mich., in 1957. Under a government contract, Dow was required to maintain 1,300-ton-per-year capacity of the plant in standby condition until 1962.

Union Carbide Metals Co., Division of Union Carbide Corp., purchased titanium tetrachloride from Colombia Southern-Chemicals Division of Pittsburgh Plate Glass Co. and produced titanium sponge metal at Ashtabula, Ohio, from 1956 to 1960 when it closed the plant due to lack of a market.

Titanium melters in 1963 were Harvey Aluminum, Inc., Torrance, Calif.; Bridgeport Brass Co. Division of National Distillers and Chemical Co., Niles, Ohio; Oregon Metallurgical Corp., Albany, Oreg.; Crucible Steel Co. of America, Midland, Pa.; Republic Steel Corp., Massillon and Canton, Ohio; and TMCA, Henderson, Nev.

Oregon Metallurgical Corp. produced ingots and castings. The other companies produced and processed ingots into mill products such as sheet, strip, plate, forging billets, and bars. Ladish Co., Cudahy, Wis., processed ingots into forged products.

The Babcock & Wilcox Co. Beaver Falls, Pa., and the Wolverine Tube Division of Calumet & Hecla, Inc., Allen Park, Mich., produced titanium pipe, tubing, and extrusions. Titanium Products Corp. produced seamless titanium pipe at Grosse Point, Mich.

Welding-Rod Coatings and Other Products

In 1963, 22 companies reported production of welding rods with titaniferous material in their coatings. There were six plants in Ohio, three in California, two each in Pennsylvania, Maryland, and Wisconsin, and one each in Tennessee, Minnesota, New Jersey, Alabama, New York, Illinois, and Michigan.

Although the companies comprising the titanium pigment metal, and welding-rod coating industries consume most titanium raw materials, there were some 70 other companies in 1963 that used titanium minerals in manufacturing ferroalloys, ceramics, fiberglass, chemicals, soap, plastics, and other miscellaneous products.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

The preferred grades of ilmenite concentrate contain from 56 to 60 percent titanium dioxide, although lower grades find a ready market. Ilmenite shipments in 1963 ranged from 45 to 60 percent titanium dioxide. In making pigment, the principal market use for ilmenite, the chromium oxide and vanadium pentoxide con-

tent should not exceed 0.2 percent and 0.5 percent, respectively.

Domestic shipments of rutile concentrate in 1958–63 averaged 95 percent titanium dioxide.

Near Jacksonville, Fla., Du Pont produced mixed products containing ilmenite, rutile, and leucoxene, averaging 60 or 80 percent TiO_2, chiefly for its own use. Data on production and use of these products are included with data on ilmenite.

Titanium slag is produced by smelting a mixture of carbon and a titanium-bearing material (usually ilmenite) in an electric furnace. The titanium dioxide content of slag produced commercially by Q.I.T. in Quebec, Canada, averages about 70 percent.

Titanium tetrachloride is a volatile colorless liquid which is used in the manufacture of titanium metal and pigments.

Titanium dioxide pigment is sold domestically in three grades. Rutile and anatase grades are more or less pure titanium dioxide, but owing to a difference in crystal structure, they differ slightly in hiding power and chalking quality. Both contain about 95 to 99 percent titanium dioxide. Extended titanium pigment containing about 30 to 50 percent titanium dioxide also is sold. According to the techniques of manufacture, the properties of titanium pigment may vary considerably as to particle size, hiding power, dispersibility, and so forth. Potential buyers are supplied detailed information concerning these properties. These data are interpreted by each user in terms of his own needs.

Titanium metal is a low-density, silver-white metal and owes its importance to a combination of lightness, strength, and resistance to corrosion. The density of titanium is 0.16 pound per cubic inch—61 percent heavier than aluminum but only 56 percent as heavy as alloy steel. Titanium alloys usually are much stronger than aluminum alloys, having tensile strength and hardness approaching that of many alloy steels. The strength-to-weight ratio below about 1,000° F exceeds that of either aluminum or stainless steel. Titanium alloys also have good impact strength and resistance to fatigue. Titanium metal is more inert than aluminum and has shown better corrosion resistance to sea water and marine atmospheres than stainless steel. It has been specified in many applications (particularly those involving resistance to chloride ion attack) where stainless steels are rapidly attacked.

The chief disadvantages are high cost, difficulties of fabrication, and excessive reactivity at high temperature. Although the melting point of titanium—3,030° F—is very high, it absorbs oxygen, nitrogen, and hydrogen and becomes brittle with prolonged atmospheric exposure above 1,000° F.

Hardness is a relative gage of the quality of titanium metal and nearly always is quoted in specifications. The hardness of most commercial titanium metal produced during the early stages of the development of the industry was quite high, being about 200 on the Brinell scale. In 1963, commercial grades ranged from 100 to 170 Brinell. Titanium metal having a Brinell hardness as low as 50 has been produced.

Titanium sponge is the metal product from reducing titanium tetrachloride with magnesium in the Kroll process. It is called sponge because of its sponge-like appearance. Sodium reduced metal also is referred to as sponge.

Titanium alloys are of three types—according to the predominant crystal phase present—alpha, alpha-beta, or beta. Aluminum is the most prominent alpha-stabilizing addition. The alpha-beta alloys also contain some aluminum, but additional elements are added to stabilize the beta phase, thus resulting in a mixed alpha-beta structure which is predominately alpha. The beta alloys also have a mixed alpha-beta structure but are predominately beta. About 20 commercial and semicommercial titanium alloys of these three types are available to the titanium user.

No uniform system has been adopted by industry for designating titanium alloys, and producers use their own designation. Specifications for titanium alloys as well as for unalloyed titanium have been summarized (*33*).[2]

TECHNOLOGY

Geology

Although titanium is estimated to be the ninth most abundant element in the earth's crust, there are only two titanium minerals, ilmenite and rutile, that are of commercial importance. Theoretically, ilmenite ($FeTiO_3$) contains a maximum of 53 percent titanium dioxide and rutile (TiO_2), 100 percent TiO_2. Titanium-bearing minerals such as anatase, leucoxene, and brookite, are associated with ilmenite and rutile and often comprise part of the marketed titanium concentrates. Many other minerals, including sphene ($CaTiSiO_5$), perovskite ($CaTiO_3$), and pyrophanite ($MnTiO_3$), are locally abundant in some deposits but have not been utilized commercially. Titanium does not exist in a metallic state in nature because of its strong affinity for oxygen and other elements.

[2] Italicized numbers in parentheses refer to items listed in the references at the end of this chapter.

Deposits containing the two main commercial titanium ore minerals, ilmenite and rutile, are found extensively throughout the world. Ilmenite, rutile, or both of these minerals have been produced commercially in the United States, Australia, Canada, Egypt, Finland, Gambia, India, Japan, Malaya, Norway, Portugal, Senegal, Sierra Leone, Spain, and the U.S.S.R.

Two types of deposits contain titanium minerals of economic importance, namely, rock and sand. Ilmenite from rock deposits and some sand deposits commonly contain 35 to 55 percent TiO_2; however, some sand deposits yield altered ilmenite containing 60 percent or more TiO_2. In anorthosite and related rocks, ilmenite is characteristically associated with iron ores, principally magnetite, but in some places, it occurs with hematite. Ilmenite in a pure state also occurs in minable rock bodies of nelsonite and schist. The most important occurrences of rutile are in beach sands, but it is found in nearly all rocks as an accessory mineral and in some rocks is concentrated enough to make them actual or potential ores.

At Tahawus, N.Y., a rock deposit outcrops on the side of Sanford Hill overlooking Sanford Lake in the Adirondack Mountains and is composed of lenticular masses of closely associated magnetite and ilmenite separated by gabbroic and anorthositic waste zones.

Dikelike nelsonite ore bodies at Piney River, Va., contain ilmenite with apatite (calcium fluophosphate) and other gangue materials and are reported to be related to a large anorthosite intrusion approximately 19 miles long by 2 to 6 miles wide. The titanium deposits of the Roseland district, Va., consist of rutile and ilmenite disseminated in a feldspar rock.

The titanium ore body at Richland Cove, Caldwell County, N.C., near Lenoir, is a dikelike intrusion in gneiss and consists of ilmenite and rutile with a micaceous gangue formed of chlorite, talc, and mica. As the rutile occurs as fine crystals within mica, only the ilmenite was recovered in past operations.

The deposits at Magnet Cove, Ark., consist of a complex mixture of igneous, sedimentary, and metamorphic rocks, many of which contain varying quantities of rutile, brookite, and ilmenite. Rutile produced from the deposit contains about 1 percent columbium.

The largest known occurrence of ilmenite in the world has been exploited at Allard Lake, Quebec, Canada. Here the ilmenite is intergrown with hematite in ore consisting of a series of narrow dikes, irregular lenses, or sill-like bodies lying within the anorthosite mass.

In sand deposits rutile and ilmenite usually occur together and may be associated with monazite, zircon, garnet, staurolite, and other minerals of high specific gravity. Titanium and other heavy minerals in Florida sands originated in schists, gneisses, and granites in the Piedmont region of the Southeastern States. The deposits are in the form of beaches, dunes, and ancient terraces. Stream deposits in the form of valley fill and alluvial fans also represent economic sources of heavy minerals in New Jersey and Idaho.

Mining and Beneficiation

The method of mining and beneficiating ilmenite depends upon whether the ore to be mined is a sand or rock deposit.

The beach and raised terrace sand deposits in Florida are mined by dredging. The alluvial deposit near Lakehurst, N.J., is mined by dragline. Both suction and bucket dredges are worked to a depth of about 60 feet. The area ahead of the dredge is prepared for mining by removing all of the trees, stumps, and trash, and at some mines consolidated overburden and ore (hard pan) was broken up by blasting. The sands contain about 4 percent heavy minerals. The proportions of heavy mineral constituents in the concentrates varied, but at one deposit in Florida the concentrate averaged about 40 percent ilmenite, 4 percent leucoxene, and 7 percent rutile. Rough concentration of the heavy minerals is done either on a barge that followed the dredge or on a portable shore plant that moved with the operation. The rough concentrate is piped or hauled by truck to the beneficiating plant. At a typical plant, Humphrey spirals are used in rougher, cleaner, and recleaner stages to produce a heavy mineral concentrate which is dewatered, dried, and separated electrostatically into conductor (titanium minerals) and nonconductor (zircon, monazite, and staurolite) fractions. The titanium fraction is separated on induced-roll magnetic machines into an ilmenite product assaying about 60 percent TiO_2 and rutile product containing about 94 percent TiO_2 (*10*).

Mining of the ilmenite-magnetite rock deposit at Tahawus, N.Y., has been by open-pit methods utilizing electric shovels for loading and 22-ton Diesel trucks for hauling the ore. Drilling in preparation for blasting required the use of a 9-inch bit with the drill holes averaging 39 feet in depth. Optimum height of the benches was 35 feet in depth (*9*). The ore, averaging 18 percent TiO_2, was crushed and ground in a number of stages by a jaw crusher, cone crusher, and rod mill to a minus 28-mesh product. Low-intensity wet-magnetic separators were used to remove a magnetic fraction. The nonmagnetic fraction, containing the ilmenite and gangue, was sized and the ilmenite was concentrated on

reciprocating tables, dried, and upgraded to a 45 percent TiO_2 concentrate on a dry magnetic separator. The magnetite fraction was sintered to make a material suitable for blast furnace feed.

At the Piney River, Va., deposit only the unconsolidated zone of residual weathering which extends to a depth of about 40 feet has been mined in the past. It was only necessary to mine the deposit several weeks each year with a power shovel to develop sufficient feed material for the beneficiating plant. The ore was concentrated and upgraded using Humphrey spirals, then the ilmenite was separated from apatite and gangue in flotation units.

Ilmenite at the Allard Lake, Quebec deposit of Q.I.T., is intimately associated with hematite so that mechanical means of separation cannot be used (*18*). The ilmenite-hematite ore was mined by open-pit techniques, crushed in jaw crusher, and shipped 27 miles by rail to Harve St. Pierre and then 550 miles up the St. Lawrence River to Sorel, Quebec. After crushing and mixing with coke, the ore was fed to electric-arc furnaces. Titanium slag, containing about 70 percent TiO_2, and iron were tapped intermittently from the furnace.

Processing

Titanium tetrachloride is made by the chlorination of a titanium bearing material in the presence of carbon. Both static-bed and fluidized-bed chlorinators are used, but all commercial plants in the United States use the fluid bed. The static-bed chlorinator requires that the feed material be briquetted or sintered before it can be used, while in the fluidized-bed chlorinator the coke and titanium materials are fed directly to the bed. The gaseous titanium tetrachloride that forms in the chlorinating unit is condensed and must be further purified before it can be utilized in making metal or pigment. Purification is usually effected by both chemical treatment and fractional distillation (*4*).

From a technical standpoint, rutile is the preferred raw material for making titanium tetrachloride; however, ilmenite, titanium slag, or products made from these materials, also can be used for this purpose.

Pigment Manufacture

Titanium dioxide of pigment quality is manufactured principally by treating finely ground ilmenite or titanium slag with concentrated sulfuric acid (*23*). All ferric iron present is reduced with iron scrap, so the iron sulfate formed is all in the ferrous state. The titanium is dissolved in water as a basic titanium sulfate, and after selective crystallization of the ferrous sulfate it is precipitated by hydrolysis, filtered, calcined to the oxide, and ground to pigment size. The original titanium dioxide pigments were of the anatase crystal modification, but in 1941 rutile pigments having greater opacity and resistance to chalking and fading were marketed. The rutile pigments also were produced from sulfate solutions by using nucleating agents.

In the chloride process for producing titanium dioxide pigments, titanium bearing materials, mixed with carbon, are chlorinated to produce titanium tetrachloride which is purified and oxidized with air or oxygen to form titanium dioxide. The chlorine is recovered from the oxidation step and recycled. Plants built in the United States since 1958 utilize the chloride process.

Metal Reduction and Fabrication

The commercially pure titanium metal produced in 1963 was made by the sodium or magnesium reduction of titanium tetrachloride. U.S. Industrial Chemicals Co. employed sodium reduction, whereas TMCA used magnesium reduction. In the magnesium reduction process, as developed by the Bureau, purified titanium tetrachloride is reduced to the metallic state in an inert atmosphere of helium or argon. Most of the magnesium chloride formed during the reaction is drained to remove it from the titanium metal and to prevent slowing of the reaction. After the reaction is complete, the reduction vessel is opened, and the mass of sponge is removed by boring on a lathe (*5*, *19*). The sponge has to be further purified to remove magnesium chloride and any residual magnesium metal by either vacuum distillation or by acid leaching (*31*).

In the sodium reduction process, the sodium is added to the reduction vessel as a liquid. The tetrachloride may be reduced in one or more stages, with the sodium chloride being removed after the final reduction. The metal made by this process is in the form of crystals or needles and is purified by leaching with water (*14*).

Electrolytic processes are being developed whereby a soluble titanium compound is electrolyzed in a fused salt bath and titanium is deposited on the cathode. In electro-refining, the metal deposited from the bath is replenished by the electrolytic dissolution of a titanium bearing anode. In electrowinning, the deposited metal is replenished by adding titanium compounds to the bath (*13*, *19*, *22*).

Major requirements for producing 1 pound of titanium sponge metal are approximately 2.5 pounds of rutile (or some other titanium material of equivalent TiO_2 content), 5 pounds of chlorine, 1.25 pounds of magnesium (or 2.5

pounds of sodium) and about 0.9 cubic foot of inert gas. If the magnesium or sodium chloride which is formed in the reduction reaction are processed to recover the metals and the chlorine, about 0.2 pound of magnesium or 0.4 pound of sodium, and 1 pound of chlorine are required. Power requirements vary from 6 to 15 kilowatt-hour per pound of sponge. The larger power requirement includes that consumed for recovering the reductant metal and chlorine.

Plant costs for producing ductile titanium metal, under 1951–54 technology, when government contracts were let, were very high. Estimates made for rapid tax amortization purposes ranged from about $15 million for a 2,700-short-ton-per-year facility to $31.5 million for a 7,500-ton-per-year facility. The average cost per annual ton of capacity was over $4,100, compared with a cost of about $1,000 to $1,500 per ton of annual capacity for aluminum.

Having produced sponge, it is necessary to carry the process further to achieve useful metal forms. Although titanium ingots can be produced by powder metallurgy techniques, nearly all commercial metal is produced by the double consumable electrode-arc melting process in an inert atmosphere or vacuum (*6*, *7*, *15*). The power requirement to produce 1 pound of titanium ingot is about 2 to 2.5 kilowatt-hours.

Titanium in the molten state has a great affinity for all gases, except the noble gases, and reacts with all known refractory materials. In addition, due to minor inclusions of salts and reductant metal, it may froth or spatter as it melts. For these reasons, to produce a contaminant-free metal, titanium is melted in a cold-cup crucible, normally of water-cooled copper. Electrodes may be of tungsten or carbon, but the industry has now converted almost wholly to the use of "consumable" electrodes, or electrodes of titanium. Use of a vacuum in the melting vessel assists in removal of dissolved hydrogen, which embrittles the metal.

In practice, the titanium sponge is compacted, with scrap metal and alloy constituents when desired, and electrodes are formed of one or more compacts; inert-atmosphere welding is used to join the compacts. The electrodes are arc-melted into a first melt ingot, which becomes the electrode for a second ingot. This double melting process, pioneered by the Bureau for zirconium and later used for titanium, insures alloy homogeneity and ingot soundness, and actually improves the yield of metal products from sponge, since the losses in forging and rejections for other reasons are reduced. The final ingot in some plants was up to 30 inches in diameter and weighed up to 8,500 pounds. Upon final conditioning by machining or by sidewall fusion, the ingots can be hot-worked by forging, extrusion, and blooming. Billets or slabs are then processed into plate, sheet, strip, bars, rods, forgings, tubes, wire, or special shapes.

Most alloy sheets are hot-rolled between steel sheets on hand mills; however, continuous hot-strip mills, Sendzimir cold rolling equipment, and vacuum annealing furnaces for processing titanium were expected to be in operation in 1964. Brake pressing and hot sizing are the most common forming methods used with titanium. Most metal removal is done with conventional machine tools, but tools must be kept sharp to avoid overheating and other good machining practices must be observed. Virtually all joining is done with Tig (trailing inert gas) methods using argon and simple shields, such as plastic bags or aluminum foil.

Complex shapes such as gate and globe valves can be cast entirely of titanium by a process developed by the Bureau (*1*, *8*). In this process the melting furnace and mold must be enclosed in a vacuum compartment to prevent contamination by gases. Both bottom-pour and tilting furnaces have been employed. Either type may utilize the skull crucible, which is so named because metal is first melted in a cold cup crucible and after the first pour a skull of solid metal is left which does not remelt in subsequent pours. Molds for titanium casting must be nonreactive and free of contaminating gases. Carbon or graphite appear to offer the most promise for industrial use.

Preparation of Welding-Rod Coatings and Other Products

Although ilmenite, slag, or manufactured TiO_2 may be used as a source of titaniferous material in welding-rod coatings, rutile is considered to be the most desirable material for this purpose and is required for certain coatings.

At one time the rods were coated by dipping them in a slurry of the coating compound; however, the rods and coatings are now extruded from a press. The ingredients are mixed in the form of slurry, then pressed into cylindrical slugs about 18 inches long and 10 inches in diameter. These slugs are put into the extruding press and the cut welding-rods, fed into the coating die, and coated to a uniform thickness by the extruded flux. The rods are dried and then fired at 1,175°.

The three major grades of master alloys of titanium with iron made for use as iron and steel additives are high-, medium-, and low-carbon ferrotitanium.

High-carbon ferrotitanium, containing 7 to 8 percent carbon and 15 to 17 percent titanium is

made by reducing ilmenite with coal or coke in a single-arc electric furnace employing a high-current density. Medium-carbon ferrotitanium containing 3 to 5 percent carbon and 16 to 20 percent titanium is made in the same fashion as low-carbon except that some rutile is added to the feed. Low-carbon-master alloys have 0.03 to 0.1 percent carbon, 20 to 45 percent titanium and are made by the aluminothermic reduction of ilmenite and rutile.

In addition, titanium scrap or offgrade sponge may be used as an alloying ingredient for steel.

Titanium carbide may be prepared by heating a mixture of rutile or manufactured TiO_2 and carbon to above 3,270° F in a vacuum or in an atmosphere of hydrogen. In one commercial process titanium dioxide, iron, and carbon are induction-heated in a graphite crucible to over 4,800° F to effect a carburization in solution. When all of the material has reacted, it is cooled and the button formed is broken up and treated chemically to remove the iron.

USES

About 99 percent of all the ilmenite consumed in 1963 and in several preceding years went into manufacturing titanium dioxide for pigments. The remainder of the ilmenite was used in making non-titanium-base alloys, carbide, welding-rod coatings, and titanium metal.

In 1963, about half of the reported consumption of rutile was for making metal and about half was for welding-rod coatings. The remainder was used for non-titanium-base alloys and carbide, and for ceramics, fiber glass, and chemicals. A significant quantity also was used for making titanium pigments, but the actual figures cannot be reported.

Titanium slag was used mainly for titanium pigments with a minor quantity being utilized in welding-rod coatings.

Since its introduction in 1916, manufactured titanium dioxide has found an expanding market in the production of paints, lacquers, plastics, paper, floor coverings, rubber, coated fabrics, textiles, and other products. The high opacity and chemical inertness of white titanium dioxide permit it to be used in almost every variety of plastic material, resin, and molding powder, except urea and thiourea mixtures. Its resistance to erosion by lactic and acetic acid makes it particularly desirable in celluloid plastics that are often treated with acetic acid, and casein, which usually contains residual lactic acid. When used as a pigment in rubber a small quantity of titanium dioxide gives a high degree of whitening, with the result that most of the desirable natural properties of the rubber can be retained.

As an opacifier in paper, the pigment is about 10 times as effective as the ordinary fillers and improves the color, brightness, and printing surface. Its properties also favor its use as a delustrant in the production of rayon.

Chemical inactivity is an important characteristic of the compound. It may be used with virtually all types of reactive vehicles; it is not discolored by most gases that may be present in the atmosphere; it does not discolor on exposure to sunlight; and it is not affected by extremes of temperature. Titanium dioxide is resistant to alkaline, acid, and saline solutions and may be used as the pigment in chemical-resistant paints of many types. It is compatible with other white and colored pigments.

Manufactured titanium dioxide also is used in welding-rod coatings, ceramics, fiberglass, and in making titanium gems.

Titanium metal has been suggested for many applications, but its major use in 1963 was for military airplanes in the airframe and powerplant. Titanium was used by airframe producers in firewalls, skin, landing-gear components, hydraulic tubing, shrouds, oil and fuel tanks, nacelle structures, fasteners, and engine supports. The major use of titanium in aircraft powerplants, such as the Pratt and Whitney J–57 engine, was in compressor disks and blades; compressor housing, and retaining rings. Fasteners also were fabricated from titanium. Producers of civilian aircraft also used titanium for similar applications to those in military craft. Commercial jet transports built in 1963 reportedly used 700 to 2,500 pounds of titanium in each airplane.

Titanium was reported to be a basic material for America's supersonic transport (SST). The SST was expected to fly at speeds between mach 2.2 and mach 3 (1,500 to 2,000 miles per hour) and use 15 to 50 tons of titanium per plane.

Titanium used in missile and space components represented about one-third of the total consumption. The Mercury spacecraft used in America's first manned orbital flight series was made largely of titanium. A double shell of the metal, supported by titanium rings and stringers was used. Titanium also was being put to wide use in the Gemini two-man spacecraft planned for the next series of manned orbital flights. The tricycle landing gear, the pressurized compartment for the crew, various pressure vessels, and the solid-fuel cases for the retrorockets were expected to be made largely of titanium and its alloys. Tankage and other components of titanium were expected to be utilized in the Lunar Excursion Module scheduled to land on the moon. Solid rocket motors, tanks, and other components for a new upper-

stage booster for the Titan III launch vehicle were being built of titanium.

Other industrial applications for titanium in the chemical and electrochemical industries represented only about 4 percent of the total market in 1963, but the base was expanding rapidly. About 50 percent of the titanium tubing employed in the process industries was for cooling wet chlorine. Other uses included anodizing racks, chlorine dioxide mixers, and pulp and paper processing equipment. Titanium was used in solutions of sodium hypochlorite, chlorate, nitric acid, sulfuric acid, and brine. Cast titanium parts such as gate and globe valves became available in 1958.

Titanium covered with a thin film of platinum is reported to be suitable for anodes in extremely corrosive solutions and as efficient as platinum at a much lower cost.

Alloys of titanium with iron, particularly ferrocarbontitanium are used in steelmaking and as an addition in cast irons. Titanium, formerly used mainly as a deoxidizer, has assumed considerable importance in the manufacture of stainless steels as a carbon- and nitrogen-stabilizing element to inhibit intergranular corrosion.

The outstanding characteristics of titanium suggests numerous other uses. These include surgical instruments, orthopedic appliances, X-ray tube targets, and textile machinery.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Rutile and ilmenite in sand deposits may be associated with zircon, monazite, garnet, staurolite, and other heavy minerals of high specific gravity. Most deposits are mined chiefly for rutile and ilmenite, and one or more of the associated minerals are recovered as byproducts; however, in some instances the titanium values are of secondary concern. For example, mining operations in Idaho were primarily for monazite, and ilmenite was recovered as a byproduct. In Malaya, ilmenite is recovered from a tailing product from tin dredging operations.

Monazite, staurolite, and zircon are coproducts of titanium mining operations in Florida. Rutile and zircon are recovered as coproducts in Australian mining operations.

ALTERNATE MATERIALS

Possible source materials other than rutile for producing titanium metal include manufactured titanium dioxide, ilmenite, and titanium slag. Manufactured titanium dioxide, which is made from ilmenite or slag, could be chlorinated readily to produce titanium tetrachloride, but manufactured titanium dioxide costs more than rutile. There are many difficulties in the chlorination of ilmenite. A large quantity of chlorine is consumed to chlorinate the iron in the ilmenite, and the iron chlorides produced have little value. Also larger chlorinating plants must be employed to produce the same amount of titanium tetrachloride from ilmenite as could be produced by a smaller plant using rutile. Aside from these economic considerations, the use of ilmenite in chlorinators presents technical problems.

The main difficulty in chlorinating commercial titanium slag has been that the magnesium and calcium compounds in the slag form a pasty mass which clogs the reaction bed. Manganese in a slag has somewhat the same effect. Other chlorine consumers in slag increase chlorine consumption over that needed for rutile with a concurrent cutback in output of $TiCl_4$. Higher grades of titanium slag will probably minimize these chlorination problems.

Ground titanium slag can be substituted for as high as 25 to 30 percent of the rutile used in welding-rod coatings and manufactured titanium dioxide can be used in some coatings if it is reprocessed to give a satisfactory particle size. However, according to the welding-rod producers there are some coatings which rutile must be used.

Manufactured titanium dioxide could be substituted for other uses of rutile, with an increase in the titaniferous raw material cost.

Selection of titanium metal over other materials of construction normally is made on a performance versus economics basis. High-strength steels, aluminum, or other metals may be substituted for titanium in many structural applications, but such substitution usually necessitates redesign and results in lower performance. In applications where titanium's corrosion resistance is a deciding factor, other metals such as stainless steel, Hasteloy, and certain nonmetals may be used, but these are often more expensive than titanium when downtime and replacement costs are considered.

SECONDARY SOURCES AND RECOVERY

About 1.25 pounds of sponge are needed to make 1 pound of mill product and in some fabricating operations, 8 pounds of mill product may be required to produce 1 pound of finished product. The excess material is scrap for which there has been a limited demand because there is enough contaminating material in the scrap to raise the hardness and brittleness of the remelted metal. Before 1954 most

of the scrap produced was accumulated as inventory, and this loss to the fabricator increased the price of the finished product.

From 1954 to 1963 the use of scrap increased as the hardness of the primary sponge decreased. In 1963, the companies that melt titanium were using 5 to 45 percent scrap in most of their melts, and in some instances ingots were made entirely from scrap.

About 50 to 60 percent of the titanium scrap generated and received by melters is remelted with sponge metal and alloying ingredients into ingot. In recent years most of the remainder has been exported, but substantial quantities are sold for various miscellaneous uses in making steel and in the chemical and electrochemical industries.

At the end of 1963 melters had 3,400 tons of titanium scrap in inventory, compared with 2,200 tons of scrap which they consumed in 1963. Additional scrap was held by farbicators and scrap dealers. A large percentage of this material was probably alloy scrap rather than commercially pure scrap. Alloy scrap has limited use due to the difficulties in sorting into various grades.

RESERVES

Ilmenite resources in rock and sand deposits in the United States, recoverable under 1963 technological conditions, are estimated to total 100 million tons. Rock deposits in New York and Virginia, containing 7 to 20 percent titanium dioxide, comprise about half of the total. The remainder is in beach sands in Florida, New Jersey and Georgia, which contain 1 to 2 percent titanium dioxide. An additional potential resource of 100 million tons of ilmenite which is not recoverable under present technological and economic conditions is found in rock deposits in California, Colorado, Minnesota, Montana, New York, Rhode Island, and Wyoming; in the ferruginous bauxite deposits of Oregon; and in sand deposits in Oklahoma.

Most of the economically recoverable resource of rutile in the United States is in sand deposits in Florida, South Carolina, and Georgia, and in rock deposits in Virginia. Little is known of their size but they probably approach 1 million or 2 million tons of contained rutile. Rock deposits in Arkansas and Virginia may contain an additional 500,000 tons of rutile which is not recoverable under present technical and economic conditions.

Titanium resources of the world were estimated to total about 2 billion tons in 1955 with a TiO_2 content of 216 million to 265 million tons. Of this quantity, the TiO_2 content of U.S. resources was 49 million to 64 million tons, or about 25 percent of the total, and the TiO_2 content of Canadian resources was 38 million to 72 million tons, or roughly 25 percent of the total. These resources included ilmenite and rutile in both commercial and submarginal deposits (*21*).

Countries having significant resources of ilmenite, recoverable under present technical and economic conditions, included Canada, India, Norway, Australia, Finland, Malaya, and the United States. Ilmenite resources in Canada, Norway, Finland and about half of those in the United States are in rock deposits. Recoverable titanium resources in the other countries are in sand deposits. Principal rutile resources, recoverable under present technological and economic conditions were in Australia, Sierra Leone, and the United States.

SOURCES OF STATISTICAL INFORMATION

The Bureau of Mines collects and publishes data on many phases of the titanium industry. Data on production, shipments, producer's stocks, and value of ilmenite and rutile concentrates are collected and published annually. Consumption and consumer stocks of ilmenite, rutile, and titanium slag also are collected and published annually.

About 35 dealers and importers of titanium ores are canvassed by the Bureau, and stocks of titanium materials held by these companies are published annually.

Production, shipments, and stocks of titanium dioxide pigment are reported annually to the Bureau by the producers of titanium dioxide. The Bureau publishes annually the percentage change in production and shipments of titanium dioxide pigments on a gross weight basis as well as the percentage distribution of shipments of pigment by end uses. The Bureau of the Census and the Business and Defense Services Administration (BDSA) collect and publish jointly the titanium dioxide content of titanium pigments produced and the stocks held by producers on a monthly basis.

Under a cooperative agreement between the Bureau of Mines, the Bureau of the Census, and Business and Defense Services Administration, monthly data are collected on the following:

consumption and stocks of titanium materials used in the production of titanium metal; titanium sponge metal production, consumption, and stocks; and titanium ingot and mill product production. The Bureau of Mines publishes quarterly data on all phases of the titanium metal industry except those concerning mill products which are published jointly by the Bureau of the Census and BDSA on a monthly basis.

The Bureau of the Census obtains monthly information on imports and exports of titanium materials including metal. The Bureau of Mines publishes import-export data on titanium materials on an annual basis.

PRODUCTION, CONSUMPTION, AND TRADE

Production

Production of ilmenite and rutile by various countries during 1954–63 are given in tables 1 and 2. The United States has been the world's largest producer of ilmenite since 1942 when disruption of seaborne imports from India made development of sources within the United States essential. Ilmenite production in Canada since 1950 includes production of titanium slag. Australia has been the world's largest producer of rutile since 1941 and accounted for 93 percent of the 1963 world total; the United States produced most of the remainder.

Statistics on the gross weight of titanium dioxide produced in the United States are not published, but the magnitude of the industry may be gaged by the data in table 3 on the titanium dioxide content of the pigments produced.

The United States has been the leading titanium metal producer in the free world since the industry was established and in 1963 produced about 80 percent of the total output. Japanese production of titanium metal has been chiefly exported to the United States, and England's output is used in its own economy. Data on world production of titanium sponge metal are shown in table 4.

TABLE 1.—*World production of ilmenite*

[Thousand short tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963
United States [1]	627	635	786	782	808	888
Canada (includes slag)	188	270	390	463	301	379
Norway	203	250	259	343	277	276
Australia (shipments)	33	94	119	186	204	224
Malaysia (exports)	87	82	132	120	114	165
Finland	99	95	92	21	96	120
Spain	9	8	12	33	46	69
Other countries	377	504	417	358	322	101
Total	1, 623	1, 938	2, 207	2, 306	2, 168	2, 222

[1] Includes a mixed product containing ilmenite, leucoxene, and rutile.

TABLE 2.—*World production of rutile*

[Short tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963
Australia	92, 584	91, 734	99, 274	113, 603	133, 497	203, 800
United States	9, 206	9, 466	8, 808	9, 045	9, 981	11, 915
India	385	429	1, 082	898	1, 770	2, 062
South Africa, Republic of	[1] 292	3, 381	3, 695	3, 483	3, 575	1, 385
Senegal	410	----------	----------	187	811	[2] 830
United Arab Republic (Egypt)	----------	1, 157	[2] 1, 100	[2] 1, 100	198	4
Other countries	323	233	241	284	168	104
Total	103, 200	106, 400	114, 200	128, 600	150, 000	220, 100

[1] 1957–58 only.
[2] Estimate.

TABLE 3.—*Production, shipments, and value of shipments of titanium pigment in the United States*

[TiO_2 content]

Year	Production (short tons)	Shipments [1]	
		Quantity (short tons)	Value f.o.b. (thousands)
1954–58 (average)	421,584	413,121	$211,962
1959	506,334	481,930	259,944
1960	455,583	468,228	252,835
1961	502,879	491,122	262,255
1962	523,201	513,822	270,438
1963	519,458	528,416	278,477

[1] Includes interplant transfers.

Source: Bureau of the Census and Business and Defense Services Administration, U.S. Department of Commerce.

TABLE 4.—*Production of titanium sponge metal, by countries*

[Short tons]

Country	1959	1960	1961	1962	1963
France (estimate)	25	25	25	30	30
Japan	2,730	2,543	2,516	1,696	1,939
United Kingdom (estimate)	350				
United States	3,898	5,311	6,727	6,730	7,879
Total	7,003	7,879	9,268	8,456	9,848

Consumption

Consumption of ilmenite and titanium slag, and rutile in 1962 and 1963 is shown in tables 5 and 6. Virtually all the ilmenite consumed is used in producing titanium pigments, and most of the titanium slag also is used for this purpose. Significant quantities of ilmenite and slag are used in welding-rod coatings. The major use of rutile in the past has been in producing welding-rod coatings, and the major peaks in the consumption of rutile for welding-rod coatings have occurred during war years. Rutile used in producing titanium metal and pigment has assumed major proportions in recent years. Data on the use of rutile in making pigment are not published to avoid disclosure of individual company data.

TABLE 5.—*Consumption of ilmenite and titanium slag in the United States*

[Short tons]

Product	Ilmenite [1]		Titanium slag	
	Gross weight	Estimated TiO_2 content	Gross weight	Estimated TiO_2 content
1962:				
Pigments (mfg. TiO_2) and titanium metal	941,954	499,471	137,576	98,195
Welding-rod coatings	503	298	453	318
Alloys and carbides	2,282	1,391	(2)	(2)
Miscellaneous	58	36	176	119
Total	944,797	501,196	138,205	98,632
1963:				
Pigments (mfg. TiO_2) and titanium metal	872,747	458,128	152,151	108,458
Welding-rod coatings	523	307	207	146
Alloys and carbides	1,659	1,036	(2)	(2)
Miscellaneous	57	35	58	41
Total	874,986	459,506	152,416	108,645

[1] Includes a mixed product containing ilmenite, leucoxene, and rutile.
[2] Included with miscellaneous.

The consumption pattern for titanium pigments is shown by the distribution of shipments to various consumers. In 1963, titanium pigments, based on gross weight, were distributed by shipments from producers as follows: Paint, varnish, and lacquers, 63.3 percent; paper 12.5 percent; floor coverings (linoleum and felt base), 4.3 percent; rubber, 4.0 percent; plastics (except covering and vinyl-coated fabrics and textiles), 2.9 percent; roofing granules, 2.1 percent; coated fabrics and textiles (oilcloth, shade

TABLE 6.—*Consumption of rutile (estimated TiO_2 content) in the United States* [1]

[Short tons]

Product	1962	1963
Titanium metal	13,126	14,021
Welding-rod coatings	14,627	16,465
Alloys and carbides	211	314
Ceramics	309	430
Fiberglass	993	915
Miscellaneous	969	1,181
Total	30,235	33,326

[1] Does not include rutile used in making titanium pigments.

cloth, artificial leather, etc.), 2.0 percent; printing ink, 1.6 percent; and ceramics 1.2 percent. In addition, 6.1 percent of the shipments were for export and to miscellaneous industries for use in welding-rod coatings, leather products, and shoe dressings.

Domestic consumption of titanium sponge metal and ingot is given in table 7. The estimated end use distribution of titanium metal is given in table 8.

Trade

Table 9 shows imports of ilmenite and rutile by country of origin. In 1952, Canada became a major external source of titaniferous material, and the United States began importing titanium slag from that country. Most of the imports of ilmenite from Canada since 1951 were in the form of slag. Almost all of the imported rutile was from Australia.

TABLE 7.—*Titanium metal in the United States*

[Short tons]

	1959	1960	1961	1962	1963
Sponge metal:					
Production	3, 898	5, 311	6, 727	6, 730	7, 879
Imports for consumption	1, 563	2, 231	2, 490	925	1, 468
Industry stocks	[1] 1, 000	[1] 1, 000	1, 200	1, 300	[1] 1, 000
Government stocks (DPA inventories)	22, 474	22, 474	22, 461	[1] 22, 436	22, 371
Consumption	3, 953	5, 487	6, 991	7, 136	8, 865
Scrap-metal consumption	1, 690	2, 527	2, 501	3, 160	2, 235
Ingot: [2]					
Production	6, 017	8, 297	9, 371	10, 400	11, 138
Consumption	5, 964	7, 978	8, 878	9, 773	10, 506
Mill shape production [3]	3, 211	5, 071	5, 647	[4] 6, 507	[4] 6, 112

[1] Revised figure.
[2] Includes alloy constituents.
[3] Bureau of the Census and Business and Defense Services Administration.
[4] Net shipments derived by subtracting the sum of producers' receipts of each mill shape from the industry's gross shipments of that shape. Data not comparable with previous years.

TABLE 8.—*End use distribution of titanium metal* [1]

[Percent]

Use	1960	1961	1962	1963
Military aircraft	65	68	60	52
Spacecraft	17	16	20	32
Commercial aircraft	13	13	12	9
Chemicals	3	3	3	4
Ordnance	2		2	2
Other				1

[1] Data based on industry estimates.

The first substantial quantity of crude titanium metal imported into the United States was from Canada (500 pounds) and France (44 pounds) in 1952. The value of the metal imported that year was $2,500. In 1953, the United States imported 10 pounds of crude metal from Canada and 71,299 pounds from Japan having a total value of $269,259. Since then Japan has become the major source of titanium imported in the United States, and virtually all of the imported metal reported in

TABLE 9.—*Titanium concentrates imported for consumption in the United States*

[Thousand short tons and thousand dollars]

Country of origin	1954–58 (average)	1959	1960	1961	1962	1963
Ilmenite:						
Canada (chiefly slag)	160	157	104	127	108	134
Australia	5	47	33	35	58	53
India	188	167	128	45		14
Other countries	6					
Total	359	372	266	207	166	201
Value	$7, 661	$7, 991	$5, 066	$5, 018	$4, 470	$5, 088
Rutile:						
Australia	41	23	28	26	36	72
Other countries	[1]	[1]	1	1	[1]	
Total	41	23	29	27	36	72
Value	$5, 362	$2, 943	$3, 611	$2, 544	$2, 646	$4, 921

[1] Less than 1,000 short tons.

table 7 came from Japan. Prior to 1963, much of the metal imported from Japan was brought in under barter agreements between Commodity Credit Corporation and Japanese producers and was placed in the supplemental stockpile.

Before 1958 imports of titanium dioxide pigment varied substantially from year to year, depending chiefly on domestic demand. However, they steadily increased from 40 tons in 1957 to 25,000 tons in 1963. The chief sources of imported pigment in 1963 were France 4,900 tons; Japan 5,100 tons; Finland 8,900 tons; and Italy, West Germany, and Spain supplied most of the remainder.

Export data for titanium products are given in table 10. Canada has for many years received most of the titanium products exported from the United States. Exports of titanium dioxide and pigments have declined in recent years, owing to construction of pigment plants in Canada.

Tariff

The tariff duties on imports of various titanium minerals and metals, effective at the end of 1963, were as follows:

Item	Rate of duty, Aug. 31, 1964	Statutory rate of duty
Titanium ore (including ilmenite and ilmenite sand).	Free	Free.
Titanium ore (including rutile and rutile sand).	do	Do.
Titanium dioxide and pigments	15 percent, ad valorem.	30 percent, ad valorem.
Titanium salts	do	Do.
Titanium metal (unwrought, and waste and scrap).[1]	20 percent, ad valorem.	25 percent, ad valorem.
Titanium metal (wrought)	18 percent, ad valorem.	45 percent, ad valorem.

[1] The duty on waste and scrap was suspended to June 30, 1964.

Source: Tariff schedules of the United States, effective A ug. 31, 1963

TABLE 10.—*U.S. exports of titanium products, by classes*

Year	Ores and concentrates		Metal and alloys in crude form and scrap [1]		Primary forms, n.e.c. [2]		Ferroalloys		Dioxide and pigments	
	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value
1954–58 (average)	1, 382	$208, 177	48	$290, 768	376	$4, 547, 152	294	$104, 382	54, 587	$19, 561, 211
1959	4, 656	289, 507	496	543, 104	499	5, 161, 074	321	145, 621	36, 282	10, 558, 287
1960	1, 260	166, 685	879	868, 846	426	3, 237, 949	245	157, 419	33, 655	10, 000, 884
1961	1, 436	190, 480	886	926, 783	384	2, 702, 322	212	93, 389	31, 104	9, 215, 839
1962	1, 224	166, 987	818	925, 495	561	4, 102, 113	130	95, 265	29, 095	8, 636, 350
1963	1, 212	176, 231	1, 261	1, 232, 245	494	3, 443, 940	211	182, 828	26, 702	8, 051, 111

[1] Beginning Jan. 1, 1955, classified as sponge and scrap; mostly scrap.
[2] Beginning Jan. 1, 1955, classified as intermediate mill shapes and mill products, n.e.c. (not elsewhere classified).

Source: Bureau of the Census.

STRATEGIC CONSIDERATIONS

Figures 1 and 2 show domestic production, imports, and consumption of ilmenite and rutile from 1941 to 1963 and graphically illustrate the degree of self-sufficiency of the United States in these minerals. The increasing trend toward greater self-sufficiency in ilmenite after 1957 is caused by declining imports of titanium slag from Canada and ilmenite from India, coupled with higher domestic production.

The United States has become progressively more dependent upon Australia for its supply of rutile. In the event of a war, the North American Continent could probably become almost self-sufficient in titanium minerals, inasmuch as ilmenite and possibly titanium slag could be substituted for rutile in the production of titanium metal.

About 90 percent of the titanium metal used in the United States is used in defense and space applications. Annual domestic capacity for production of titanium sponge metal in 1963 was about 14,000 tons, but with the 1964 closing of the Du Pont plant, capacity will drop to about 10,500 tons, compared with the 8,900 tons consumed in 1963. Of the total new supply of titanium sponge metal in 1963, 16 percent was imported, chiefly from Japan.

GOVERNMENT PROGRAMS

Through the Office of Minerals Exploration (OME) in the Department of the Interior, the Government loans up to 50 percent (limited to $250,000 for any one contract) of the costs of exploration for rutile.

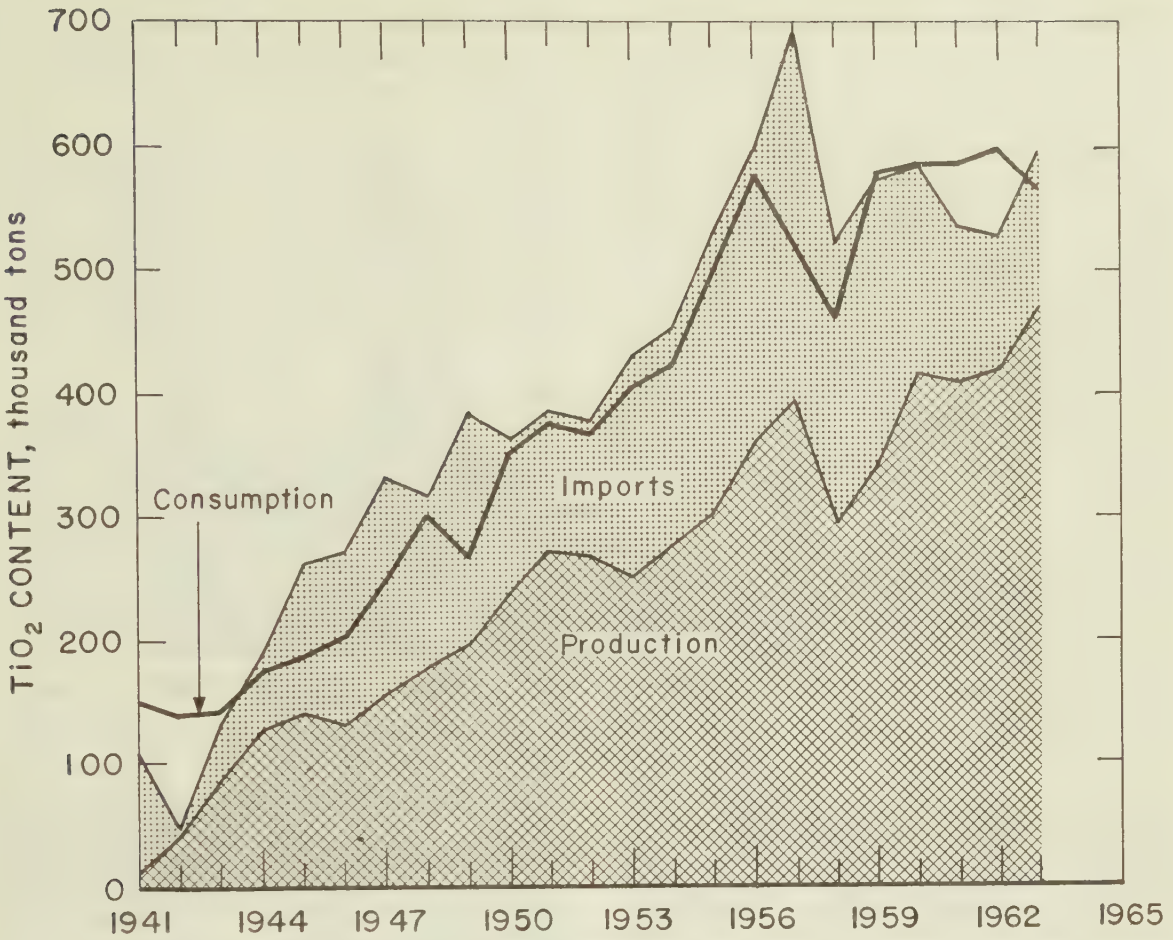

FIGURE 1.—Domestic Production, Imports, and Consumption of Ilmenite (Includes Titanium Slags and Mixed Product).

The Defense Production Act of 1950, as amended, provided authority to develop the productive capacity of the domestic economy to a level sufficient to meet existing demand and to provide a basis for full mobilization in event of a defense emergency. Titanium metal, however, was in an extremely rudimentary stage of development, and the setting of relatively high expansion goals practically required the establishment of a whole new industry. Various agencies concerned utilized nearly all the expansion aids available. Expansion incentives employed included advancement of funds and commitments to purchase output; accelerated tax amortizations; grants for research and development; and revolving inventory funds.

Overall responsibility for the titanium expansion program rested in the Office of Defense Mobilization; however, other government agencies were delegated to handle various operational functions of the program.

The first expansion goal for titanium sponge was set in March 1951 with an initial goal of 7,200 tons. By 1954, this was expanded to 35,000 tons per year. In September 1955, the sponge goal was reduced to 22,500 tons, which was the capacity already contracted for, and the goal was accordingly suspended.

Rutile was the only titanium mineral included in the National Stockpile List of Strategic and Critical Materials in 1963, and no other titanium minerals have been purchased by the Government for stockpiling purposes.

Titanium sponge metal was acquired by the Government from domestic producers through Defense Production Act contracts and from Japanese producers in exchange for surplus agricultural products through the barter program, administrated by the Commodity Credit Corporation (CCC), Department of Agriculture.

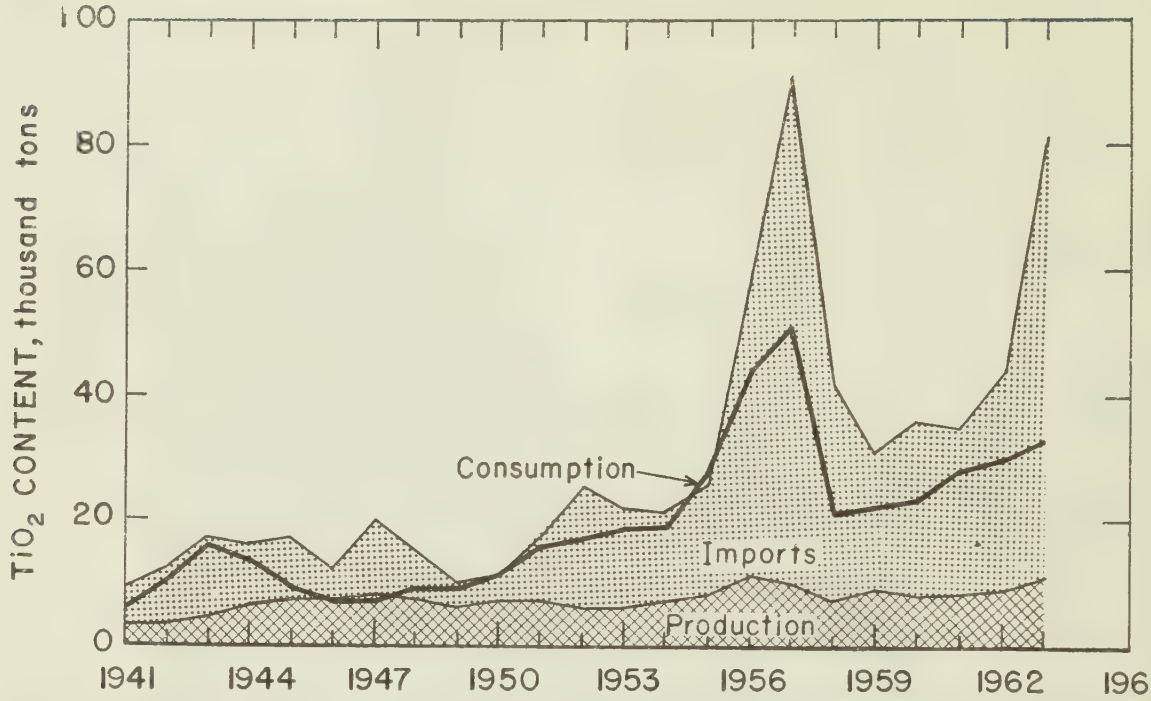

FIGURE 2.—Domestic Production, Imports, and Consumption of Rutile (Excluding That Used in 1961 Through 1963 for Making TiO_2 Pigment).

On June 30, 1964, government inventories of rutile totaled 47,600 tons, of which 18,600 tons was in the national (strategic) stockpile, 17,400 in Defense Production Act stocks, and 11,600 tons in the supplemental stockpile. In addition, stocks of titanium sponge totaled 31,400 tons, of which 22,400 tons was in DPA stocks, and 9,000 in the supplemental stockpile.

PRICES

The average year-end prices for ilmenite and rutile, which were Government-stabilized during World War II at $29 per long ton and $180 per short ton, respectively, declined to $15 per long ton and $80 per short ton by 1950. In the early 1950's increased demand for ilmenite for making pigment and new requirements for rutile for making titanium metal resulted in price increases to $20 per long ton and $250 per short ton by 1955. The decrease in rutile requirements for metal in the late 1950's caused the price to drop to the 1950 level by 1959. However, increased demand for rutile for making chloride pigment which started in 1958 caused the price to rise to $104 per short ton by 1963. Ilmenite prices rose from the 1955 level to $28 per long ton, then declined to $24.50 per long ton in 1958, the price which was in effect at the end of 1963.

The price of titanium sponge has decreased significantly since 1954. In 1948 commercial titanium sponge sold for about $5 per pound. At the end of 1963 prices quoted for various grades of titanium sponge metal ranged from $1.27 to $1.60 per pound.

Prices of titanium mill products also have shown a steadily decreasing trend, and averaged base prices for commercially pure sheet have ranged from $15 to $20 per pound in 1950 to $4.90 to $5.10 per pound at the end of 1963. Prices per pound quoted for titanium mill products f.o.b. mill, commercially pure grades in lots of 10,000 pounds were as follows:

Sheet	$4.90–$5.10
Strip	4.90– 5.10
Plate	3.80– 4.00
Wire	3.50– 3.80
Forging billets	2.40– 2.55
Hot-rolled bars	3.15– 3.35

Prices of titanium pigment have increased from the Government stabilized price of 14½ to 16½ cents per pound for anatase and rutile grades during World War II to 25½ to 28½ cents per pound at the end of 1963. Calcium-rutile base pigments containing about 30 percent TiO_2 increased from 5½ cents per pound to 9⅞ cents per pound during the same period. The half-cent-per-pound price differential on shipments of one company's titanium pigment to users west of the Rocky Mountains was eliminated in 1963. Some reductions of the

base prices was given to purchasers of large lots.

The following prices were quoted in the Oil, Paint and Drug Reporter at the end of 1963:

	Price
Anatase, Chalk-resistant, regular and ceramic, carlots, delivered, per pound	$0.25½
Less than carlots, delivered, per pound	.26½
Rutile, nonchalking, bags, carlots, delivered East, per pound	.27½
Less than carlots, delivered East, per pound	.28½
Titanium pigment, calcium-rutile base, 30 percent TiO_2, bags, carlots, delivered, per pound	.09⅜
Less than carlots, delivered, per pound	.09⅞

TAXES

The Internal Revenue Code of 1954 included for the first time a depletion allowance for ilmenite. The code states that for Federal Income Tax purposes the allowance of deduction for depletion of ilmenite, rutile, and other ores containing titanium, mined from deposits in the United States, was 23 percent of the gross income providing that this was not greater than 50 percent of the net income from the property.

RESEARCH

Studies to improve the recovery of titanium minerals from ores have emphasized development of electrostatic and flotation processes. A substantial amount of research has been directed toward development of economic methods to produce a product from ilmenite having a high titanium dioxide content that can be chlorinated as easily as rutile. These studies have centered on pyrometallurgical techniques (*3*, *12*) and acid leaching processes at high pressures and temperatures. Direct chlorination of ilmenite has been studied by the Bureau (*24*, *25*).

Development of the chloride process for making titanium pigment has led to increased industrial research to improve the purity and grain size distribution of pigment made by the sulfate process.

Titanium metal has been produced commercially only since 1948, and a large number of research and development projects by government, industry, universities, and private institutions have attempted to solve the many problems encountered in the production and use of the metal. The Bureau was instrumental in interesting private industry in the metal and in helping to solve many of the production and processing problems involved in its manufacture. The Bureau's publication Material Survey, Titanium, (*21*) contains a detailed discussion of the extensive research and development program of Government and private industry through 1954. Since that time research has focused on improvements in the commercial process using magnesium or sodium to reduce titanium tetrachloride (*19*) and development of electrorefining and electrowinning processes (*13*).

Direct reduction of titanium ores to titanium metal using carbon, calcium, magnesium, aluminum and other reducing agents has been studied by many investigators. With the exception of calcium reduction, these processes have yielded an impure metal product which has to be further refined to produce pure titanium.

Titanium semifabricators and about 60 fabricating firms, which include airframe and jet engine manufacturers, conduct the major research projects on producing end-items of titanium metal. Projects underway in 1963 included studies on methods of vapor deposition, and cladding of titanium, adhesive bonding, and high-energy rate forming.

Emphasis in the Bureau titanium research program was on fused salt electrowinning processes. Other studies by the Bureau included investigations of mineral resources, mineral dressing techniques, extractive processes, analytical methods for high-purity titanium, thermodynamic properties, and development of melting and casting techniques.

OUTLOOK

Titanium resources in rock deposits are far greater than in sand deposits. However, about half of the world's titanium mineral output comes from sand deposits. This 50–50 relation of the sources of titanium minerals probably will continue for many years because the quality of titanium minerals which can be recovered from sand is higher and mining costs are lower; however, the long-range trend is toward fuller utilization of the more plentiful rock deposits. One or more of the large rock deposits of titanium minerals in Colorado, Wyoming, Arkansas, Rhode Island, or Virginia may be developed commercially before the 1980's. Additional sand deposits may be developed in the Pacific Northwest, Oklahoma, and the Southeastern States.

Australia, Canada, and India probably will continue to supply about 25 percent of the domestic demand for ilmenite and titanium slag; however, in an emergency the entire demand could be met by domestic and Canadian sources.

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It is likely that the United States will become increasingly dependent on Australian and African sources for rutile.

The average annual rate of increase in demand for titanium dioxide pigment in the United States during 1950–63 was almost 5 percent. This growth rate is expected to continue through 1980, resulting in requirements for about 800,000 tons of titanium dioxide in 1970 and about 1.2 million tons by 1980. The relative importance of imported material, which represented 4.5 percent of the total new supply in 1963, is expected to increase to about 8 percent of the total supply by 1970, and 15 percent by 1980. Thus the TiO_2 content of titanium materials required in the United States for pigment manufacture would be approximately 850,000 tons, and 1.1 million tons, respectively, in 1970 and 1980, assuming a 90 percent recovery of TiO_2 from all raw material sources.

It is expected that industry development of the chloride process for making titanium dioxide pigment by oxidation of titanium tetrachloride will continue to expand. From a technical standpoint rutile is the preferred raw material for making the tetrachloride, but because of its relative scarcity, ilmenite and titanium slag also may be used for this purpose.

Projected demand in thousand short tons for the various titanium raw materials for pigment production is as follows:

	1963	1970	1980
Ilmenite	873	1,100	1,100
Titanium Slag	152	185	300
Rutile	(1)	170	340

[1] Figure withheld to avoid disclosing individual company confidential data.

It is likely that ilmenite or titanium slag will be used in the chloride process by 1970 and is almost certain that they will be used by 1980. This would increase the estimates for ilmenite and titanium slag and decrease the estimates for rutile.

The pattern of consumption of titanium material in welding-rod coatings in past years indicates that this use will continue to increase at about the same rate as the national economy and will require about 23,000 tons of rutile annually by 1970 and about 35,000 tons by 1980. During periods when rutile is in short supply, which may occur as demand for making titanium tetrachloride increases, ilmenite, titanium slag and manufactured TiO_2 will be used to some extent in place of rutile in welding-rod coatings.

Miscellaneous uses of titanium compounds such as alkali titanates and titanium borides, carbides, chlorides, and organics in the chemical, electrical, and machine tool industries should expand at about the same rate as the national economy.

The large research effort to develop materials of construction for aircraft and spacecraft, underwater vehicles, and use in the chemical industries, indicates that titanium metal has a bright future. Titanium's lightweight, high strength, and corrosion resistance has made it a highly desired material in the space industry; in supersonic transports (SST) and other high performance aircraft; in deep diving submarines; and in chemical equipment used in highly corrosive media.

The relatively short history of the titanium metal industry, which was considerably influenced by government programs in the early stages of development, provides little basis for projecting its future use. However, it is significant that despite the marked decline in demand for titanium sponge metal following the curtailment of the manned military aircraft program in the mid-1950's and cessation of the Government's purchasing program for the metal in 1958, the average growth rate of the industry from its start in 1948 to 1963 was about 15 percent per year. During 1959–63, the growth rate was about 20 percent per year, chiefly because of expanding applications in high-performance airplanes, missiles, and spacecraft.

Use of titanium metal in the rapidly growing space industry is expected to continue at an increasingly higher rate; however, it may be that large numbers of spacecraft will not be necessary for many years. Consequently, the rate of increase in this application may level off or even decline in the 1970's when the range of development problems under study may not be as broad as in 1963. Conversely, the effect of many of the potentially large uses of titanium such as those anticipated in the SST program and underwater craft, which were in early development stages in 1963, is not likely to be fully realized prior to the 1970's.

Industry estimates of the future growth of titanium metal demand range from 10 to 15 percent per year. It seems probable that the lower rate will apply to 1970, resulting in demand for about 17,000 tons of sponge metal in that year. Inasmuch as chemical uses should continue to grow and some potentially large uses may not materialize until the 1970's, it is estimated that the higher rate would apply after 1970 resulting in demand for about 70,000 tons in 1980. Requirements for rutile, or some other titaniferous material of equivalent TiO_2 content, would be about 34,000 and 140,000 tons, respectively, in 1970 and 1980.

PROBLEMS

Expansion of the pigment and other segments of the titanium industry requires development of sources in sand or rock deposits and efficient methods of mining, recovering and upgrading the titanium values. The rock deposits have a higher titanium content than sand deposits and usually are larger, but the mineralization is considerably more complex. Utilization of many titanium deposits is complicated by the presence of vanadium, chromium, manganese, columbium, or tantalum in the titanium minerals. No method has been developed in the United States to use titanium minerals such as sphene, perovskite, and ulvospinel which are abundant in several large rock deposits.

Mining problems encountered in developing the rock deposits of titanium minerals are those common to open-pit bench mining in both altered and unaltered feldspathic rock. Owing to the hard and abrasive nature of the overlying rock at one mine, and overburden to ore ratio of only 1½ to 1 can be handled. The attitude of the deposit is such that the minable depth is thus limited to about 600 feet. Tests at this mine also have demonstrated a need for information on rock fragmentation, especially as related to blasting pattern. Dredging or drag-line excavating of the sand deposits, which normally are substantially lower in grade than the rock deposits, necessitate the handling of large quantities of abrasive sands. Large quantities of clay and other slime forming materials present in some sand deposits create a problem of expansive treatment and disposal or storage.

Enough rutile may not become available to meet the expanding demand for titanium tetrachloride for titanium pigments and metal. Therefore, economic processes need to be developed for chlorinating ilmenite or for making a high TiO_2 content product that is suitable for chlorination or for use directly as a pigment. If chlorination of ilmenite or other high iron materials is to become commercial, a use for the byproduct iron chloride must be found. A similar problem is encountered in the production of TiO_2 by the sulfate method—only part of the iron sulfate byproduct is utilized and the remainder constitutes an expensive waste and disposal problem.

High production costs of titanium metal stem from the fact that it must be made from very pure substances under carefully controlled conditions. The Kroll process, which is currently used, is a batch process, and although many improvements have been made it is unlikely that the method can be made continuous. Research indicated that the electrolytic process may be adaptable to continuous operation; however, numerous problems remain to be solved. For example, molten titanium cannot be obtained electrolytically, nor have suitable processes for electroplating the metal been developed. The metal is deposited as crystal, necessitating periodic cathode removal and replacement in an inert atmosphere and reclaiming of entrapped carrier salt. Moreover, the highly reactive titanium salts cause serious corrosion problems. Further complications result from the necessity to separate the anode and cathode compartments. These problems, coupled with the need for devices for continuously adding the feed and changing cathodes under a controlled atmosphere necessitate a complicated cell design.

To utilize titanium it must be melted under vacuum or an inert atmosphere. Its high chemical reactivity also complicates the selection of refractory materials for crucibles and molds, and this is a major deterrent to development of efficient melting and casting processes.

The problems in fabricating titanium can for the most part be traced to its unusual flow characteristic. More energy is required to form titanium than most steels. Excessive springback makes it difficult to cold form titanium to specifications. Some of the high-strength alloys must be formed while hot and have to be protected during the operation. Anisotropy is a problem with certain titanium alloys.

The upper limit of the serviceability of titanium alloys is about 600° C. To achieve maximum advantage of titanium in design of airplanes and spacecraft this thermal limit must be raised. In addition, sheet alloys are needed in thin gages and larger sections than have hitherto been available. Other important potential applications will require the joining and forming of large sections of titanium plate, which are difficult or impossible under present technology.

Engineering data on corrosion properties and in-plant performance of titanium are needed to enable potential users in the chemical and marine industries to determine the service life and long-range costs for titanium equipment.

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TUNGSTEN

By Richard F. Stevens, Jr.[1]

TUNGSTEN metal, because it has the highest melting point, has become an important structural material in nuclear and space applications requiring resistance to extremely high temperatures. Historically, tungsten metal has been used in lighting and electrical applications; tungsten carbides have been used in metal-shaping tools, in rock bits, and in hardfacing applications where resistance to wear is required.

Although the production rate has varied widely during the past 40 years, domestic production of tungsten concentrate has been equal to approximately two-thirds of domestic consumption. As a result of increased demand during the Korean war and of Government stockpiling beginning in 1951, domestic production increased from less than 1,500 tons, tungsten metal content, in 1949 to nearly 8,000 tons in 1955. Following the termination of stockpile purchases in December 1956, production was severely curtailed. Although domestic production increased to slightly over 4,000 tons in 1961 and 1962, production in 1963 was significantly lower due to the low market price of tungsten and the oversupply of tungsten from mainland China which was sold in Europe at well below the world price. About 60 percent of the domestic output since 1900 has come from California and Nevada, but in recent years, substantial quantities of tungsten have also been produced in Colorado, North Carolina, Montana, and Idaho.

Mainland China, United States, Burma, Bolivia, Portugal, and Korea have been the leading producers, and the United States, United Kingdom, France, Germany, Sweden, and U.S.S.R. have been important consumers. Commercial-grade tungsten minerals are found primarily in quartz veins and contact-metamorphic scheelite. Other commercial occurrences have been found in replacement, placer, and pegmatite deposits. Both underground and opencut methods are used in tungsten mining operations. Tungsten concentration operations, primarily gravity and flotation methods, are usually conducted at or near the mine site. Tungsten concentrate is refined to metal powder by chemical processing followed by hydrogen or carbon reduction of the tungsten compounds. Ferrotungsten is produced primarily in the electric furnace.

Current tungsten applications are based on the extreme hardness and wear resistance of tungsten carbides; on the ability of tungsten and tungsten alloys to retain hardness at elevated temperatures; and on the high melting point, high density, low vapor pressure, and favorable electrical and thermionic properties of pure tungsten. An important objective of current research is the development of coatings and alloys to allow fuller utilization of the exceptional high-temperature properties of tungsten in reactor and aeronautical structural applications. Its melting point of 3,410° C (6,170° F) is higher than that of any other metal, and it has superior mechanical properties at high temperatures.

The measured, indicated, and inferred domestic resources range in grade from 0.3 to 1.0 percent tungsten trioxide (WO_3) and contain over 70,000 tons of tungsten metal. The domestic supply of tungsten is more than adequate for short-term requirements. For the long term, however, adequacy of supply at reasonable cost is uncertain.

Although world tungsten resources are widespread, by far the largest reserve occurs in mainland China. The free world reserve (excluding mainland China, North Korea, and the U.S.S.R.) is estimated at about 295,000 tons, tungsten metal content. Reserves in mainland China, North Korea, and the U.S.S.R. may be about four times as great as those in the free world.

Free world production of tungsten in 1963 was estimated at slightly over 11,000 tons, metal content. Of this quantity, about 4,000 tons (domestic mine shipments plus imports) was supplied to the United States and about 7,000 tons was available to other free world countries. U.S. consumption (11.1 million pounds contained tungsten in 1963) is estimated at 30 to 50 percent of free world consumption.

[1] Commodity specialist.

Problems of the tungsten industry include: Establishing an adequate resource base to meet future requirements; the balancing of a stable peacetime production with consumption; improving quality of products and reducing costs by the use of improved mining and processing procedures; and developing of coatings and alloys to allow more effective use of the special properties of tungsten. The latter relates to the need for materials in the nuclear and space industries capable of withstanding extremely high temperatures.

BACKGROUND

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Records show that from 1905 to 1954 mainland China produced about 28 percent of the world's tungsten. The United States produced 13 percent, Burma 10 percent, Bolivia 8 percent, Portugal 8 percent, and Korea 7 percent. Recent data on tungsten production in China are not available, but the productive capacity of free world sources was greatly increased in the 1950–56 period, largely because of the U.S. Government stockpiling program. Free world production was estimated at 9,000 tons, metal content, in 1949, 25,000 tons in 1956, and nearly 14,000 tons in 1958. U.S. sources of supply in recent years are shown in table 9.

Domestic mines and mills in the past 40 years have produced concentrate containing more than 80,000 tons of tungsten, equal to about two-thirds of consumption during the same years. Production ranged from none in 1921 and 1922 to a peak of nearly 8,000 tons in 1955 when output was reported from 700 mines. Consumption and prices also have varied widely.

Most of the output has come from a relatively few large mines. In 1955, 48 percent of the Nation's production came from the 5 largest mines, 73 percent came from the 10 largest, 82 percent from the 15 largest, and 92 percent from the 40 largest. Thus, about 650 other producers supplied only about 8 percent. In 1963 the two major producers accounted for over 90 percent of the domestic shipments.

Crude tungsten ores are nearly always treated at or near the mine site by gravity and/or flotation methods which produce a market-grade concentrate, a low-grade concentrate (requiring chemical treatment), or both. In 1955 and 1956, three principal chemical plants in the United States treated low-grade concentrate on a custom basis. These plants were located near Bishop, Calif., at Salt Lake City, Utah, and at Glen Cove, Long Island, N.Y. The latter plant was established chiefly to treat imported concentrate.

In 1963 ferrotungsten was manufactured by three firms in the United States, but substantial quantities were imported. Hydrogen reduced tungsten powder was produced by eight firms and carbon reduced powder by two firms. Chemicals were produced as coproducts at some of the above plants and as chief products at some others. The geographic locations of domestic producers of tungsten concentrate and principal producers of tungsten products are given in table 1.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

A short ton unit of WO_3 (tungsten trioxide) is equivalent to 1 percent of a short ton, or 20 pounds of WO_3, and contains 15,862 pounds of tungsten metal (W). A short ton of concentrate with 60 percent WO_3 contains 60 short ton units equivalent to 1,200 pounds of WO_3 (951.72 pounds of tungsten metal). In foreign countries, tungsten is measured in long ton units (22.40 pounds of WO_3), metric ton units (22.046 pounds of WO_3), or in other units. The WO_3 may be contained in scheelite, $CaWO_4$; ferberite $FeWO_4$; huebnerite, $MnWO_4$; or wolframite (Fe, Mn) WO_4 concentrate.

Synthetic scheelite ($CaWO_4$) is used for the same purposes as other tungsten concentrates. This compound results from a chemical process used for upgrading concentrates low in tungsten, for chemical cleaning of impure concentrates, or from processing scrap.

Scheelite concentrate for direct addition to steel melts is usually high grade and low in certain undesirable impurities. The following specification is typical for this use:

		Percent by weight
Tungsten trioxide (WO_3)	minimum	70.00
Tin (Sn)	maximum	.10
Copper (Cu)	do	.05
Arsenic (As)	do	.10
Antimony (Sb)	do	.10
Bismuth (Bi)	do	.25
Molybdenum (Mo):		
Class A steels	not specified	-----
Class B steels	maximum	.80
Phosphorus (P)	do	.05
Sulfur (S)	do	.50
Manganese (Mn)	do	.50
Lead (Pb)	do	.10
Zinc (Zn)	do	.10

TABLE 1.—*U.S. producers of tungsten concentrate and principal producers of tungsten products in 1963*

Company	Location of mine, mill or processing plant	Major products produced
Climax Molybdenum Co., Division of American Metal Climax, Inc.	Lake County, Colo. Coldwater, Mich., Langeloth, Pa.	Tungsten concentrate.
Union Carbide Nuclear Co., Division of Union Carbide Corp.	Pine Creek, Inyo County, Calif.	Chemicals, Ammonium paratungstate (APT).
Tungsten Mining Corp	Vance County, N.C	Tungsten concentrate.
A & B Metal Manufacturing Co. Inc	Houston, Tex	Crushed cast carbide powder.
Adamas Carbide Corp	Kenilworth, N.J	Carbide powder, made from hydrogen reduced tungsten powder.
Oregon Metallurgical Corp	Albany, Oreg	Ingots and other mill products.
Allegheny Steel Co	Ferndale, Mich	Carbide powder, made from hydrogen reduced tungsten powder.
Chem-Met	Clinton, Md	Scheelite produced from scrap.
Cleveland Tungsten, Inc	Cleveland, Ohio	Metal powder—hydrogen reduced.
Diamond Metal Division, Reed Roller Bit Co.	Houston, Tex	Carbide powder, crushed cast.
Fansteel Metallurgical Corp	North Chicago, Ill	Metal powder—hydrogen reduced, chemicals.
Firth Loach	McKeesport, Pa	Carbide powder made from hydrogen reduced tungsten.
General Electric Co	Euclid, Ohio	Chemicals, metal powder—hydrogen reduced.
General Electric Co., Metallurgical Products Department.	Detroit, Mich	Carbide powder made from hydrogen reduced tungsten.
General Electric Co., Lamp Metals & Components Department.	Cleveland, Ohio	Ingots, rod, wire, and other mill products.
Hughes Tool Co	Houston, Tex	Crushed cast carbide powder.
Kennametal, Inc	Latrobe, Pa	Carbide powder made from hydrogen reduced tungsten, carbide powder—crystalline.
M & R Refractory Metals, Inc	Springfield, N.J	Metal powder—hydrogen reduced, tungsten metal pellets.
McCaine Metal Co	Houston, Tex	Crushed cast carbide powder.
Metal Carbides Corp	Youngstown, Ohio	Carbide powder—made from hydrogen reduced tungsten.
Molybdenum Corporation of America	Washington and York, Pa.	Ferrotungsten, chemicals.
Nevada Scheelite, Division of Kennametal, Inc.	Fallon, Nev	Crystalline carbide powder.
Newcomer Products, Inc	Latrobe, Pa	Carbide powder made from hydrogen reduced tungsten.
Stoody Co	Whittier, Calif	Crushed cast carbide powder.
Sylvania Electric Products, Inc	Towanda, Pa	Chemicals, metal powder-hydrogen reduced, billet, rod, wire, and other mill products.
Union Carbide Metals Co., Division of Union Carbide Corp.	Niagara Falls, N.Y	Ferrotungsten, hydrogen and carbon reduced metal powder.
Vascoloy-Ramet Corp	Waukegan, Ill	Carbide powder made from hydrogen reduced tungsten.
Victor Equipment Co	Norwalk, Calif	Crushed cast carbide powder.
Wah Chang Corp	Glen Cove, N.Y	Ferrotungsten, metal powder-hydrogen reduced, chemicals (APT).
Wah Chang Corp., Albany Division	Albany, Oreg	Ingots and mill products.
Westinghouse Electric Corp	Bloomfield, N.J	Metal powder—hydrogen reduced, ingots and mill products.
Willey's Carbide Tool Co	Detroit, Mich	Carbide powder made from hydrogen reduced tungsten.

Copper, arsenic, antimony, phosphorus, sulfur, and manganese are the impurities that are most often a problem in meeting the specification. Some scheelite contains chemically combined copper and/or molybdenum which can be removed only by chemical decomposition and precipitation. Synthetic scheelite, if nodulized, is an ideal product for direct addition to steel, but unnodulized material of fine particle size is not desirable because of high dust losses. Natural scheelite concentrate of the all-slime type is not wanted in this use for the same reason. Concentrate of the black-ore (wolframite type) minerals is not satisfactory in steel manufacture because of its manganese content.

Hydrogen-reduced tungsten metal powder is the intermediate product from which tungsten metal (wire, rod, sheet, etc.), and cemented tungsten carbides are produced. It is also used for making tungsten alloys. Carbon reduced tungsten metal powder is the intermediate product used principally in the manufacture of cast carbides and in alloys. Both types of metal powder result from the reduction of chemically produced oxides of tungsten.

Tungstic acid, sodium tungstate, ammonium paratungstate, and tungstic oxide are chemical forms produced at intermediate stages in manufacturing metal powder.

The national stockpile specification shown in table 2 is for concentrate to be consumed in chemical-type plants. This specification is not as rigid as those of some industrial users because of the difficulty in obtaining high-grade concentrate in the quantity required for the stockpile. Nearly all plant managers prefer concentrate containing 70 percent or more WO_3. Some report that scheelite concentrate containing more molybdenum and phosphorus than the maximum listed in table 2 is satisfactory, but producers of filament wire call for a maximum molybdenum content of 0.025 to 0.002 percent.

TABLE 2.—*National stockpile specification for tungsten concentrate*

Constituents	Chemical requirements, percent by weight (dry basis)			
	Type A, B, or C—ferberite, huebnerite, or wolframite ores and concentrates		Type D—natural scheelite ores and concentrates	Type E—synthetic scheelite precipitates
	For carbide powder	Pure metal		
Tungsten trioxide [1] (WO_3)—minimum	65. 00	65. 00	65. 00	65. 00
Tin (Sn)—maximum	1. 50	1. 50	. 10	. 05
Copper (Cu)—do	. 50	. 50	. 10	. 05
Arsenic (As)—do	[2]. 20	[2]. 20	. 10	. 05
Bismuth (Bi)—do	. 50	. 50	. 25	. 25
Antimony (Sb)—do	. 05	. 05	. 10	. 05
Molybdenum (Mo)—do	. 10	. 025	. 10	. 10
Phosphorus (P)—do	. 05	. 05	. 05	. 05
Sulfur (S)—do	. 50	. 50	. 50	. 50
Lead (Pb)—do	1. 00	1. 00	. 10	. 10
Zinc (Zn)—do	1. 00	1. 00	. 10	. 10
Calcium (Ca)—do	. 20	. 20	----------	----------
Manganese+iron (Mn+Fe)—do	----------	----------	2. 00	. 50

[1] Corrected for columbium and tantalum, if present.
[2] Maximum, 0.1 percent arsenic for processed Government-owned material returned under beneficiation contracts.

Molybdenum, antimony, and to a less extent bismuth are objectionable because they pass through the process unaffected and appear in the end product. Arsenic, phosphorus, and sulfur interfere with the process but do not contaminate the end product. Tin, copper, and manganese, which are detrimental in high-speed steel, are not detrimental at chemical-type plants.

Antimony attacks the "boats" used for reducing tungsten compounds in the hydrogen-reduction furnaces, and is undesirable in filament wire for electronic purposes. Some firms specify maximum antimony in concentrates at 0.005 percent; others as much as 0.05 percent.

Many consumers will not accept concentrate higher than 0.02 percent in arsenic or more than 0.05 percent in phosphorus; nearly all plants will reject concentrate containing more than 0.25 percent of combined arsenic and phosphorus. These elements, frequently present in the original ore and in imported concentrate, are objectionable in the manufacture of both steel and chemicals.

Ferrotungsten is a crude alloy of tungsten and iron consumed in manufacturing alloy steel. The standard specification by industry (American Society for Testing and Materials (ASTM) Specification A 144–50) and the Government (National Stockpile Specification P–57a–R2) are the same; they are summarized as follows:

a. Chemical requirements: Ferrotungsten shall meet the following chemical requirements:

	Percent
Tungsten	70 to 80
Carbon—maximum	. 60
Manganese—do	. 75
Phosphorus—do	. 06
Sulfur—do	. 06
Silicon—do	1. 00
Copper—do	. 10
Arsenic—do	. 10
Antimony—do	. 08
Tin—do	. 10
Sum of arsenic, antimony and tin—do	. 20

b. Physical requirements: Ferrotungsten shall be furnished crushed to a size 1 inch and less.

The consuming firm also specifies the maximum molybdenum content allowable; this is often set at 0.6 percent if tungsten tool steels are being produced.

TECHNOLOGY

Geology

Tungsten-bearing ore and concentrate are of two principal types; calcium tungstate, comprising the first three minerals listed in table 3, of which scheelite is by far the most important; and iron-manganese tungstates comprising the last three.

TABLE 3.—*Commercially important tungsten minerals*

Mineral	Composition	Formula	Tungsten, percent
Scheelite	Calcium tungstate	$CaWO_4$	63.9.
Powellite	Calcium tungsto-molybdate.	$Ca(Mo,W)O_4$	Not fixed.
Cuprotungstite	Copper tungstate	$Cu_2(WO_4)(OH)_2$	45.
Ferberite	Iron tungstate	$FeWO_4$	60.6
Wolframite	Iron-manganese tungstate.	$(Fe,Mn)WO_4$	60.6 to 60.7.
Huebnerite	Manganese tungstate.	$MnWO_4$	60.7.

The iron-manganese tungstates form a continuous series from the iron to the manganese end. The name wolframite is often applied to the entire series, but arbitrary splits are made at 20–80 and 80–20 mole-percent to ferberite, the iron-rich end member, and huebnerite, the manganese-rich end member. Together, the wolframites are known as "black ore."

Tungsten-bearing minerals listed below have not been significant sources of tungsten.

Minerals	*Formulas*
Ferritungstite	$Fe_2O_3 \cdot WO_3 6H_2O$.
Tungstite	$WO_3 \cdot H_2O$.
Russellite	$Bi_2O_3 \cdot WO_3$.
Stolzite	$PbWO_4$.
Raspite	$PbWO_4$.
Chillagite	$Pb(W,Mo)O_4$.
Tungstenite	WS_2.
Sanmartinite	$(Zn,Fe,Ca)WO_4$.
Anthoinite	$Al(WO_4)(OH) \cdot H_2O$.

Most commercial tungsten occurrences have been found in quartz veins and in contact-metamorphic deposits, but replacement, pegmatite, and placer deposits have also been productive. Tungsten mineralization is nearly always associated with siliceous granitic rocks; the distribution of tungsten minerals is typically irregular.

In the United States, vein deposits in Vance County, N.C., and Lemhi County, Idaho, have been important as sources of huebnerite and in Boulder County, Colo., as sources of ferberite. Lesser quantities of scheelite also occur in these deposits.

Contact-metamorphic deposits supply about 75 percent of the U.S. total production, but worldwide they are less important than vein deposits. Scheelite occurs sporadically in the metamorphic rock (tactite) at or near contacts between limestone and the intruding granitic rocks. Important deposits of this type occur at the Pine Creek and Black Rock mines in California. Other scheelite deposits occur in Nevada and in Montana.

A hydrothermal replacement deposit at the Yellow Pine mine in Idaho was a major producer of tungsten in World War II. Stibnite and gold were associated with scheelite in a brecciated quartz monzonite.

Weathered outcrops and placer deposits have been important in some areas. However, they usually are not large or far from the source. Tungsten minerals are friable and rather soluble and may be leached from an ore body without being redeposited. More than 8 million units, at a very low concentration, are contained in the brine of Searles Lake, Calif.

Huebnerite is disseminated in the molybdenum ore of the Climax mine in Colorado. Even though the huebnerite content of the ore is very low, substantial tungsten production is achieved as a coproduct because of the large-scale mining operation.

In many deposits tungsten is the only valuable mineral; other deposits contain tungsten-tin, tungsten-molybdenum, tungsten-antimony, tungsten-silver-gold, tungsten-copper, and tungsten-silver-copper-lead-zinc. Tin and tungsten minerals occur together in mainland China, Burma, Malaysia, Thailand, Bolivia, Brazil, Portugal, Spain, and other countries. Important occurrences of tungsten associated with molybdenum are found in the United States at the Pine Creek mine of Union Carbide Nuclear Co., in California and the Climax mine of American Metal Climax, Inc., in Colorado.

Mining

Mining methods have ranged from primitive to highly mechanized. Only a few tungsten mines (probably no more than one or two in the United States) have produced as much as 1,000 tons of ore per day on a continuing schedule.

By far the largest production has come from underground mines using conventional methods such as shrinkage, square set, open stope, room and pillar, and various adaptations. In 1955, about 20 percent of domestic output came from open pit and placer operations, but in 1963 all output came from two underground operations.

Beneficiation

Crude ore mined and milled in the United States in 1955 and 1956 averaged about 0.5 percent WO_3, and the lowest grade was not much below 0.3 percent. Virtually all of the tungsten produced in 1963 was a coproduct of molybdenum mining.

Gravity methods of concentrating the relatively heavy tungsten minerals have been used most frequently. The specific gravities of scheelite, huebnerite, and ferberite are 6.10, 7.12, and 7.51, respectively. Small mills may employ only crushing and grinding equipment, jigs, and tables. Recovery at such plants averages 60 to 70 percent, but the product is often a good grade concentrate. The high losses caused by the tendency of tungsten minerals to slime during grinding have led to many modifications in flowsheets and equipment.

Flotation processes have gained importance since about 1930, and most modern, large-scale mills use these in combination with gravity methods. Well-equipped mills recover more than 90 percent of the tungsten mineral content, but though part of the product may be high grade, a substantial part is low-grade concentrate requiring chemical treatment.

If calcite and apatite are the principal contaminants, the low-grade concentrate may be brought up to market specifications by acid leaching; a number of tungsten mills in operation during 1955–57 used this procedure. But much low-grade concentrate is shipped from mills to chemical plants to produce market-grade synthetic scheelite. Tungsten concentrate (as low as 5 percent WO_3) is dissolved in sodium carbonate solution under pressure at some plants and by lixiviation after sintering or fusing with sodium salts at others. Calcium chloride is added to the solution to precipitate calcium tungstate; in some instances, molybdenum is first removed from the solution by precipitation as molybdenum sulfide. The pressure method is said to be less costly than sintering if concentrate containing less than 20 percent WO_3 is treated, and more costly if a higher grade feed is used. In either circumstance, the cost is appreciably more than production of a tungsten concentrate by gravity-flotation methods.

Roasting, magnetic separation, or electrostatic separation may also be used to improve the product grade. Separation of scheelite from wolframite, required by some consumers, is accomplished by magnetic separation.

A Bureau of Mines Report (*18*)[2] summarized the milling practice and chemical treatment methods at most of the major and many of the smaller domestic tungsten operations in 1956.

Refining and Preparation of Products

The flow sheet shown in figure 1 indicates the methods of treatment of tungsten ores and concentrate used to obtain industrial products. Most tungsten concentrate is converted to ferrotungsten, metal powder, or other intermediate products before being consumed in end uses. Some scheelite however is used as such in steelmaking. For this use, synthetic or natural scheelite of suitable grade requires no processing except that it is usually nodulized to minimize dust losses.

In producing ferrotungsten, concentrate is reduced in electric furnaces, with carbon or silicon as the reducing agent, or it may be made by aluminothermic or metallothermic methods. A batch-type operation is necessary because the high melting point of ferrotungsten precludes tapping. Any tungsten mineral, or combination of minerals, can be used provided the iron-tungsten ratio will permit formation of an alloy containing 70 percent or more of tungsten. Through the control of slag types and the high temperatures involved, producers of ferrotungsten can lower the impurity content and can therefore use concentrate that would not meet specifications for direct charging to steel.

Ferrotungsten (about 78 percent W), melting base (about 35 percent W), scrap high in tungsten content, and high-purity scheelite (both natural and synthetic) are all used for charging tungsten to steel. Metal powder, pellets, and certain proprietary compositions are also used. Ferrotungsten is used commonly when tungsten tool steels (6.75 to 22 percent W) are manufactured; however, some firms use only the other tungsten products listed above when molybdenum, chromium, and miscellaneous tool steels (less than 6.75 percent W) are produced. Tungsten tool steels require a low-molybdenum content in the charge; most molybdenum tool steels require several percent molybdenum. This is important to producers of tungsten concentrate that contains molybdenum; nearly every use of tungsten, except charging to molybdenum, chromium, and miscellaneous tool steels, requires a product low in molybdenum.

In general, the higher the percentage of tungsten desired in the steel, the greater the need for ferrotungsten. However, the recent trend has been toward the low-tungsten-content steels, and less ferrotungsten has been used, relative to total tungsten consumption.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

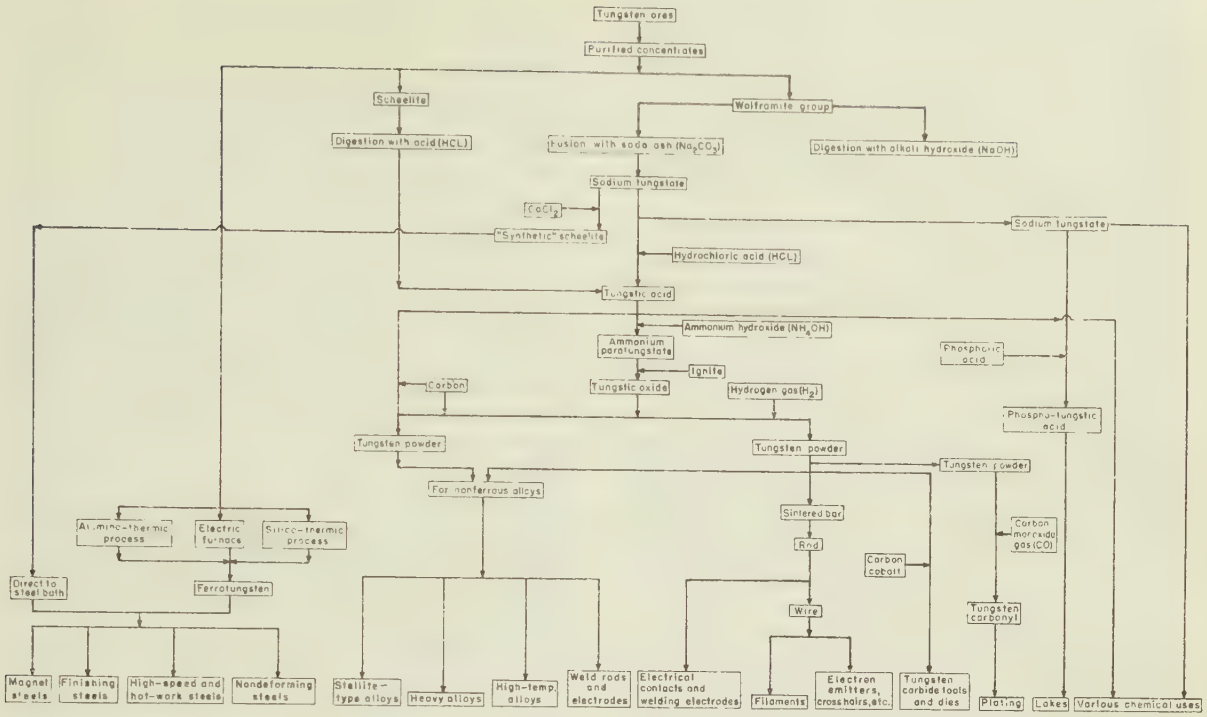

FIGURE 1.—General Treatment of Tungsten Ores and Concentrates to Industrial Products.

In manufacturing tungsten metal powder, the concentrate is treated by chemical methods to produce compounds which are then reduced to metal by hydrogen or carbon. The processes vary according to raw materials, product specifications, and plant design. Methods designed for treating wolframite-type minerals are not satisfactory for treating scheelite and vice versa.

In treatment of wolframite-type concentrate, a typical procedure may include:

(1) Decomposition of the concentrate with sodium hydroxide (NaOH) solution, under pressure or in open tanks; or fusion with sodium carbonate (Na_2CO_3) followed by leaching with water.

(2) Filtering and reaction of the filtrate, containing sodium tungstate, with hydrochloric acid to form a tungstic acid (H_2WO_4) precipitate; or evaporation of the filtrate to form sodium tungstate crystals; or treating the filtrate with calcium chloride ($CaCl_2$) to precipitate calcium tungstate ($CaWO_4$). Additional steps in each of the two latter cases would convert the tungsten to tungstic acid precipitate.

(3) Conversion of the tungstic acid to the oxide by ignition or by treatment with ammonia (NH_4OH), to produce ammonium paratungstate which is converted to the oxide by thermal decomposition.

(4) Reduction of the tungstic oxide to tungsten metal powder, using either carbon or hydrogen as a reductant.

In treating scheelite, concentrate decomposition is accomplished with hydrochloric acid. The resulting tungstic acid precipitate may then be dissolved either in ammonium hydroxide or sodium hydroxide to produce the corresponding tungstate solution, and subsequent steps are similar to those outlined above.

Hydrogen-reduced tungsten powder is produced from ammonium paratungstate or tungstic oxide placed in iron or nickel boats and pushed through tubes counter to a flow of hydrogen. Heat is applied to the outside of the tubes. Grain size of the metal powder product is a primary consideration in its use for manufacturing pure tungsten or tungsten carbide products. Particle size of the metal powder is directly related to particle size of the oxide from which it is reduced and is also partially dependent on temperature and time of reduction. For example, if other variables are suitably fixed, a maximum of 800° C produces a particle size (mean diameter) of 0.5 micron whereas a maximum of 1,200° C produces a particle size of 10 microns. The reduction rate also increases with higher temperatures, resulting in greater furnace capacity for production of coarse powder than for production of fine powder.

Carbon-reduced powder is produced from tungstic acid in crucibles or in tubular furnaces similar to those used for hydrogen reduction. Lampblack is the usual reductant in crucibles; natural gas or manufactured city gas is the reducing agent in tubular furnaces. Skill is required to produce a powder low in carbon and of a satisfactory grain size.

Tungsten chemicals used for manufacturing pigments are produced as coproducts at some plants or they may be the chief product. Quantitatively this is not an important phase of the tungsten industry.

Because of the difficulty encountered in fabricating tungsten mill products, the production of tungsten wire, rod, and sheet is based primarily on hydrogen-reduced powder metallurgy procedures although recently tungsten has also been successfully prepared by arc-melting techniques. The powder is compressed, sintered, heated to incipient fusion by passage of an electric current, swaged, and drawn or rolled.

Cemented (or sintered) carbides are usually made from hydrogen-reduced tungsten powder. The powder is carburized, compacted with a cobalt binder into the desired shape, and sintered. Grain size and cobalt content are important factors in determining hardness and other properties. Mixed carbide powders containing titanium carbide or tantalum carbide or intermetallic compounds such as $WTiC_2$ are also used. Crystalline tungsten carbides, made directly from concentrate, are gaining in use.

Cast (or fused) tungsten carbide is made mostly from carbon-reduced tungsten powder and scrap. These are melted, together with a carbonaceous material, and cast into shapes for use as such, or for crushing and use as a hardfacing material.

USES

The major uses of tungsten can be divided into four end-use categories: In alloys, chiefly alloy steels; in carbides (cemented or cast); as a pure or substantially pure metal; and in various chemical compounds. The consumption of tungsten products by end use, as reported to the Bureau of Mines in 1963, is shown in table 4.

Hardness at elevated temperatures is the important property possessed by tungsten alloys such as high-speed tool steels, die and hot-work steels and other special alloys. The greatest use is in the shaping of metal by high-speed drilling, cutting, milling, etc., or by hot-forming methods. Wear and abrasion resistance, shock resistance, corrosion resistance, and increased strength, at elevated temperatures are other properties of tungsten-bearing steel alloys. The standard types of high-speed and hot-work tool steels are listed in table 5.

Alloys of cobalt, chromium, and tungsten have been used to a large extent as hardfacing materials and for cutting and shaping of metals. They retain a higher hardness at temperatures above 1,100° F than the best high-speed steels. Tungsten alloys are increasingly being used for structural applications in temperature environments of 1,700° F or higher. Valve steel, turbine blades, and vessels for containing high temperature materials are examples of this use. Six alloys that have been developed for high temperature applications are listed in table 6.

Other alloys include tungsten-silver and tungsten-copper compositions for electrical contacts and welding applications and "heavy metal" alloys for high-density applications such as counterweights or shielding. The density of tungsten is 19.3. Heavy metal, about 90 percent tungsten and 10 percent copper or copper-nickel is also used as a high-strength material for applications such as boring bars.

Cemented (or sintered) tungsten carbide is used for cutting edges, in dies, for machine parts subject to wear, and in similar applications where extreme hardness is desirable. The largest use is in machine tools, but large quantities are also consumed by the mining industry as carbide-tipped rock bits. Most often the carbide component is a small insert, razed or clamped to the cutting edge, but there is a trend toward the use of solid carbide tools. During World War II and the Korean war, large quantities of tungsten carbide were used in armor-piercing shells.

Cast (or fused) carbide is used principally as a hardfacing material. In one such application, crushed and sized particles are encased in a hollow steel tube which, when applied as a welding rod, melts to form a matrix for the carbide particles. Cast carbide is also used in dies and in some wear resistant parts.

Pure or substantially pure tungsten is important in electric lighting, electronics, and electrical contact applications. Its melting point, 3,410° C (6,170° F) is higher than that of any other metal and its vapor pressure is lower. Some tungsten is used for welding electrodes, some for shielding, and some for X-ray tube components. Tungsten heating elements are used extensively to vaporize certain metals ("metalizing" plastic name plates, etc.). The filament of electric lamps and the distributor points of automobiles are well-known uses of tungsten. Metallic tungsten coatings applied by various methods, such as flame spraying and vapor deposition, are increasing in importance. Tungsten carbonyl, $W(Co)_6$, has been used to produce acid-resistant linings for cast iron and steel pipes.

TABLE 4.—*Consumption of tungsten products, by end uses, in 1963*

[Thousand pounds of tungsten content]

End use	Ferrotungsten, melting base, self-reducing tungsten, tungsten sponge mix, etc.	Carbon-reduced tungsten powder [1]	Hydrogen-reduced tungsten powder [2]	Tungsten carbide powder		Chemicals	Scheelite (natural or synthetic)	Scrap	Total	Percent of total
				Made from metal powder	Crystalline and crushed cast					
Steel:										
High speed	611	45					1,084	129	1,869	18
Hot work and other tool	290	14					185	51	540	5
Alloy (other than tool) [3]	238	10	3				130	74	455	4
High-temperature nonferrous alloys [4]	58	102	34				173	195	562	6
Other nonferrous alloys [5]	13	7	132	5	233	224	3	124	741	7
Tungsten metal:										
Wire, rod, and sheet			1,276						1,276	12
Other		1	718						719	7
Carbides:										
Cemented or sintered			40	2,284	1,069			65	3,458	33
Other (including cast or fused)	3	61	38	19	599			32	752	7
Chemicals [6]						144			144	1
Total	1,213	240	2,241	2,308	1,901	368	1,575	670	10,516	100
Stocks at consumer plants Dec. 31	299	44	665	160	6	220		204	1,598	

[1] Includes tungsten metal pellets that may be hydrogen or carbon reduced or scrap.
[2] Does not include quantities consumed in making tungsten carbide powder.
[3] Includes steel mill rolls, stainless, and other alloy steels.
[4] Includes cutting and wear-resistant alloys.
[5] Includes diamond drill bit matrices, electrical contact points, and welding rods.
[6] Includes fluorescent powders and organic and inorganic pigments.

TABLE 5.—*Shipments of high-speed and hot-work tool steel (excluding hollow drill steel)* [1]

Type	Carbon	Chromium	Vanadium	Tungsten	Molybdenum	Cobalt	1959	1960	1961	1962	1963
	High-speed tool steel (composition, percent)						Shipments (short tons)				
Molybdenum types:											
M2, M8	0.80	4.00	2.00	6.00	5.00		8,395	6,412	6,571	8,088	7,778
M3, M4	1.00–1.30	4.00	2.70–4.00	5.50–6.00	4.50–5.00		1,176	1,060	975	1,264	1,208
M1, M7	.80–1.00	4.00	1.00–2.00	1.50–1.75	8.00–8.75		5,235	4,741	4,233	5,270	4,573
M10	.85	4.00	2.00		8.00		2,510	1,779	1,451	2,193	2,355
M6, M15, M30, M34, M35, M36, other M	.80–1.50	3.75–4.00	1.15–5.00	1.50–6.50	3.50–9.50	5.00–12.00	614	578	613	1,137	1,471
Tungsten types:											
T1, T2, T3, T7, T9	.70–1.20	4.00	1.00–4.00	14.00–18.00			1,640	1,293	1,094	1,126	1,240
T4, T5, T6, T8, T15	.75–1.50	4.00–4.50	1.00–5.00	12.00–20.00		5.00–12.00	691	617	593	726	680
Total							20,261	16,480	15,530	19,804	19,305
	Hot-work tool steel (composition, percent)						Shipments (short tons net)				
Chromium types: H11, H12, H13	.35	5.25	0.40–1.00	0–1.35	1.50		11,370	8,978	9,811	10,479	9,891
Tungsten types: H20, H21, H22, H23, H24, H25, H26	.25–.50	3.00–12.00	.40–1.00	9.50–18.00			893	660	559	659	575
Miscellaneous types: H14, H15, H16, H41, H42, H43	.35–.63	3.60–5.25	.28–1.90	0–6.40	0–8.70		1,208	1,417	1,493	1,647	1,548
Total							13,471	11,055	11,863	12,785	12,014

[1] Annual Statistical Report American Iron and Steel Institute, 1963.

TABLE 6.—*Tungsten-bearing alloys for high-temperature applications*

	TPA valve steel	Cyclops 17W	S-816	NA-22H (Blaw Knox)	X-40 (stellite 31)	L-605 (stellite 25)
Principal usage	Exhaust valves in aircraft engines.	Turbo supercharger blades and disks.	Jet engine blades	Furnace supports	Jet engine blades	Combustor components in jet engines.
Form	Wrought	Wrought	Wrought	Cast	Cast	Wrought.
	COMPOSITION					
Tungsten	3.0	4.0	4.0	5.0	7.5	15.0.
Carbon	0.50	0.50	0.50	0.50	0.50	0.15 maximum.
Chromium	12.0	15.0	20.0	28.0	25.0	20.0.
Nickel	12.0	15.0	20.0	48.0	10.0	10.0.
Molybdenum			4.0			
Columbium			4.0			
Cobalt			45.0		Balance	Balance.
Iron	Balance	Balance	5.0 maximum	Balance	2.0 maximum	2.0 maximum.

Tungsten chemicals are used in textile dyes, ink, paints, enamels, and glass manufacture. Because of the luminescence of certain tungsten compounds and their derivative phosphors, they are used in luminescent pigments. They are also used in X-ray screens and television picture tubes. Tungsten phosphors are used in fluorescent lighting.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Tin and molybdenum minerals are the most important byproducts of tungsten mining and conversely tin and molybdenum mines are the most important sources of byproduct tungsten.

Other byproducts or potential byproducts of tungsten mining include pyrite, antimony, copper, bismuth, lead, zinc, fluorspar, gold, silver, and beryllium. However, tungsten mining has not been an important source of byproduct metals. A potential byproduct source of tungsten is the brine of Searles Lake, Calif.

ALTERNATE MATERIALS

Molybdenum, to a large extent, is substituted for tungsten in tool steels. Titanium or other carbides and sintered aluminum oxide are used in some applications to replace tungsten carbides. The use of transistors in place of vacuum tubes may reduce the need for tungsten in electronics; fluorescent lighting has reduced the importance of electric-lamp filament.

SECONDARY SOURCES AND RECOVERY

Industry returns to producing plants its tungsten-bearing steel scrap. Scrap is also saved at producing wireworks, and sold or returned to the chemical processing units. Tungsten carbide and tungsten metal sludge from grinding are usually reclaimed by chemical treatment to produce synthetic scheelite or they may be used in production of cast carbides. Imports of scrap increased from 200,000 pounds in 1953 to more than 400,000 pounds in the first half of 1956. Subsequent scrap data are not available. A relatively high price for concentrate and suspension of duty 1953–56 contributed to the increase of imports.

High-temperature alloy scrap is potentially an important source of tungsten and other elements, but most alloy scrap consumption in the United States has been confined to remelting without separation of the constituent elements.

RESERVES

The domestic reserve of tungsten ore was estimated in 1957 at about 9 million short ton units of WO_3 equivalent to about 142.5 million pounds of contained tungsten (*15*). Recent data have indicated that this figure may be conservative. Domestic tungsten reserves are shown in table 7.

It is estimated that an additional 8.5 million short ton units of WO_3 are present in the brine solutions of Searles Lake, Calif. If an economic method of recovering this tungsten is developed, the domestic reserves might be doubled. However, this source is not considered to represent a tungsten reserve under present technology.

At the 1963–64 price level, virtually all the domestic tungsten deposits are submarginal except where production is as a byproduct or coproduct of another marketable mineral.

Although the largest world tungsten resource is in mainland China, few data, other than what can be implied by observing China's tungsten trading practices, are available on recent developments there, in the Soviet Union, or in North Korea. Although an estimate of world reserves is given in table 8, commercial reserves in 1963 were substantially less because of the decline in prices caused by the disposal of large quantities of tungsten, believed to be from mainland China, at prices well below the world quotations.

CONSERVATION

Mining and benefication research have contributed to the improved recovery of tungsten minerals. Better mining equipment and mining practice and use of flotation and leaching processes have made possible the exploitation of lower grade deposits.

Past scarcities and high cost of tungsten have tended to restrict its use and promote the use of substitutes. Tungsten requirements for tool steel have been reduced by the use of small carbide inserts at cutting edges. Collection and use of scrap are well established and are becoming increasingly important.

SOURCES OF STATISTICAL INFORMATION

Data on production, shipments, consumption, and stocks of tungsten concentrate are published by the Bureau of Mines in monthly and annual reports. Export and import data are collected by the Bureau of the Census. Data on consumption of tungsten in tool steel are published by the American Iron and Steel Institute.

The Statistical Summary of the Mineral Industry, a British publication, contains data on foreign shipments. The Statistical Yearbook

of the United Nations and publications of foreign countries contain additional statistical information.

TABLE 7.—*Tungsten reserves of the United States, by grade of ore, 1955*

[Thousand short-ton units of WO_3]

Grade	Measured and indicated	Inferred
1.0 percent WO_3 plus	130	120
0.5 to 1.0 percent WO_3	3,200	3,800
0.3 to 0.5 percent WO_3	900	850
Total	4,230	4,770
0.01 to 0.10 percent WO_3 [1]		5,500

[1] Submarginal ore (from part of which production can be made as byproduct).

TABLE 8.—*World tungsten reserves in 1954*

[Estimated units of tungsten trioxide in measured, indicated, and inferred ore]

Country	Thousand short-ton units WO_3	Country	Thousand short-ton units WO_3
Argentina	500	Mexico	100
Australia	1,600	Nigeria	Small
Bolivia	5,500	Peru	550
Brazil	2,500	Portugal	2,000
Burma	4,800	Southern Rhodesia	100
Canada	1,000	Spain	650
China, mainland	134,500	Sweden	Small
France	150	Tanganyika	Small
Cambodia	300	Thailand	500
Japan	100	United Kingdom	400
Korea	7,000	U.S.S.R.	1,700
Malaysia	1,400	United States	9,000

PRODUCTION, CONSUMPTION, AND TRADE

Consumption of tungsten in the United States has exceeded domestic production except 1953–56; imports have exceeded domestic production in all but 13 years between 1919 and 1963. Sources of domestic production and import sources for 1959–63 are shown in table 9.

Complete data on world consumption of tungsten are not available, but in 1952 it was estimated that the United States with 49 percent, United Kingdom 20 percent, West Germany 9 percent, France 8 percent, and Sweden 3 percent, accounted for 89 percent of free world consumption. In more recent years, the United States consumption has been between 30 and 50 percent of the total. No estimate is included for the U.S.S.R. although consumption there is believed high in view of the availability of tungsten from China and the relative scarcity of molybdenum in that country. U.S. consumption 1959–63 is given in table 9.

Although the domestic mining industry has operated continuously (except for 1921 and 1922) for more than 50 years, rate of production has varied widely due, in part, to changing military requirements, and the Government stockpiling program. Only a few domestic producers have been able to compete consistently on the open market with foreign pro-

TABLE 9.—*Salient tungsten statistics*

[Thousand pounds of contained tungsten]

	1954–58 (average)	1959	1960	1961	1962	1963
United States:						
Mine production	[1] 12,948	[2]	6,669	8,188	8,280	[2]
Mine shipments	10,307	3,473	6,972	7,847	8,021	5,384
Consumption	7,186	9,835	11,605	11,128	13,691	11,061
Imports, general	17,350	6,248	5,178	2,744	3,709	3,882
Imports for consumption, by country:						
Argentina	1,110		142		59	398
Australia	1,472	685	716	415	405	185
Bolivia	3,307	735	451	203	721	942
Brazil	1,888	1,144	560			
Burma	406	195	128			85
Canada	1,448				[3]	
Congo (Leopoldville)[4]	590	314	113	62		
Korea, Republic of	2,238	798	225	805	1,491	846
Mexico	488	28	1		[3] 1	[1] 96
Peru	966	311	66	29	202	35
Portugal	1,241	780	1,017	468	915	435
Spain	966	53	8	39	80	
Thailand	422	105				
Other countries	724	287	98	102	156	38
Stocks:						
Producer	[1] 1,672	[2]	2,402	2,667	3,004	3,313
Consumer and dealer	3,834	3,196	3,143	3,212	3,054	2,934
World: Production [5]	69,571	58,245	68,714	73,663	69,760	61,576

[1] 1958 not included to avoid disclosing company confidential data.
[2] Figure withheld to avoid disclosing company confidential data.
[3] Mexico and Canada.
[4] Formerly Belgian Congo.
[5] Partially estimated.

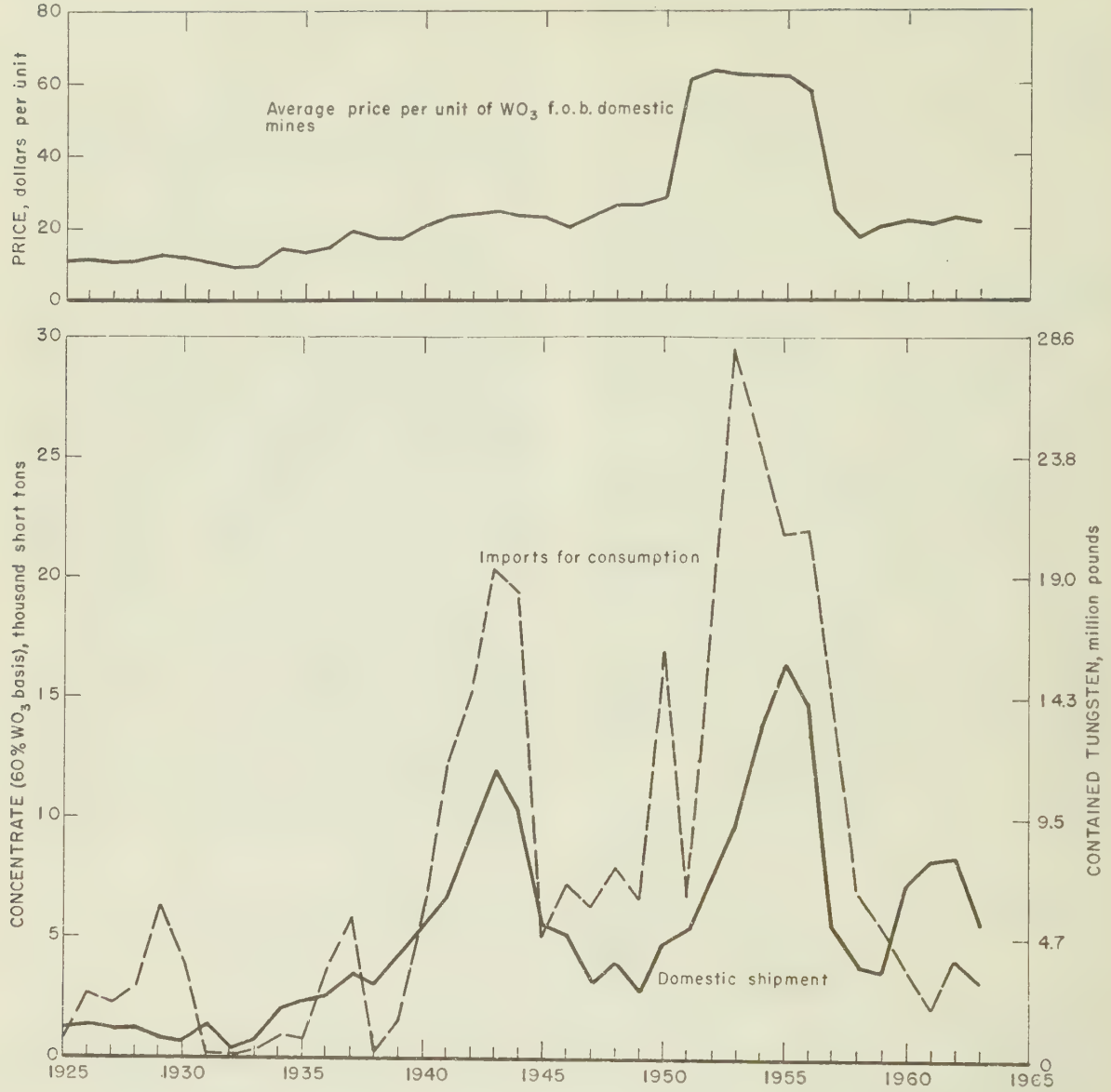

FIGURE 2.—Domestic Mine Shipments, Imports, and Average Price of Tungsten Concentrate.

ducers. Exports of concentrate have been negligible. Domestic mine shipments are shown in figure 2.

The duty on tungsten ore and concentrate under the "Tariff Schedules of the United States, Annotated (1963)" is 50 cents per pound of tungsten content (equivalent to $7.93 per short ton unit of WO_3) as indicated in table 10. Under TSUS the statutory Rates of Duty for tungsten are:

Ore and concentrate	50 cents per pound.
Ferrotungsten	60 cents per pound + 25 percent ad valorem.
Metal, carbide and combinations	60 cents per pound + 50 percent ad valorem.
Ingots and shot	50 percent ad valorem.
Sheet, wire, or other forms	60 percent ad valorem.

STRATEGIC CONSIDERATIONS

A large domestic productive capacity, under a sufficient price incentive to assure supply for the national stockpile, was demonstrated in the 1950–56 period. Current stockpiles have been deemed adequate for emergency requirements. However, it is probable that imports will con-

TABLE 10.—*Import duties on tungsten products*

Commodity	Tariff rate in—			
	Act of 1930	1948	1951	1963
	Cents per pound of metallic tungsten			
Tungsten ore and concentrate	50	[1] 38	[2] 50	50.
	Cents per pound of tungsten content plus percent ad valorem			
Tungsten metal, tungsten carbide, and mixtures or combinations containing tungsten metal or tungsten carbide, all the foregoing in lumps, grains, or powder.	60 plus 50 percent	42 plus 25 percent [3]	42 plus 25 percent [3]	42 plus 25 percent.
Tungstic acid and all other compounds of tungsten, n.s.p.f.	60 plus 40 percent	42 plus 25 percent [3]	42 plus 25 percent [3]	42 plus 20 percent.
Ferrotungsten, ferrochromium tungsten, chromium tungsten, chromium cobalt tungsten, tungsten nickel, and all other alloys of tungsten, n.s.p.f.	60 plus 25 percent	42 plus 12½ percent.[3]	42 plus 12½ percent.[3]	42 plus 12½ percent.
	Percent ad valorem			
Forms containing more than 50 percent tungsten or tungsten carbide:				
Ingots, shot, bars, or scrap	50	[3] 30	[4] 25	[5] 21.
Wire	60	[3] 40	[4] 30	[5] 25½.
Sheets or other forms	60	[3] 40	[4] 30	[5] 25½

[1] General agreement (Geneva). Rate effective May 22, 1948.
[2] Effective Dec. 11, 1950.
[3] General agreement (Geneva). Rate effective Jan. 1, 1948.
[4] General agreement (Torquay). Rate effective June 6, 1951.
[5] Effective June 30, 1958.

NOTE.—Public Law 869, 81st Congress, suspended the duty on scrap metal (including tungsten) until July 1, 1951. This suspension was continued to July 16, 1956, when it was reimposed by Public Law 723, 84th Congress.

tinue to comprise a substantial portion of U.S. supply because of economic factors favoring foreign producers.

Termination of U.S. Government stockpile purchases was followed by closure of nearly all tungsten mines in the United States, and many in the free world, but, many of these mines continue to represent potential sources of supply. Although the largest proportion of world reserves is in mainland China, the widespread tungsten occurrences are an important strategic factor, and production also comes from many different countries.

Tungsten is a strategic material because of its use in the tools of production. The machine-tool and mining industries, especially, rely on tungsten, and demand rises sharply during periods of expanding industrial production. Possibly of equal importance, but requiring a smaller tonnage, is the use of tungsten in lamp filaments and electronics. Tungsten and tungsten-base alloys for use at elevated temperatures have become important in the nuclear and space industries. Although the current volume of tungsten in these applications is relatively small, it is expected to increase significantly.

GOVERNMENT PROGRAMS

Stockpile purchase of tungsten concentrate was authorized under the Strategic and Critical Materials Stock Piling Act (Public Law 520 approved July 23, 1946) and the Defense Production Act of 1950 (Public Law 774, approved September 8, 1950). Purchase of concentrate from domestic producers was terminated in December 1956, and the last contract for acquisition of foreign concentrate was fulfilled in 1959. On June 30, 1964, Government inventories totaled 80,400 tons, of which 51,900 tons was in the national (strategic) stockpile, 26,300 in DPA stocks, and 2,200 in the supplemental stockpile.

Under the Defense Minerals Exploration Administration, a program beginning in April 1951, provided exploration loans up to 75 percent of the cost. This program, for tungsten, ended on September 11, 1958.

Government policies have played an important role in the history of the domestic tungsten industry. Imposition of a tariff in 1922 was a factor in increasing the domestic component of U.S. supply. Rapid increase in scrap imports occurred during suspension of the duty on scrap. Price controls, as with other commodities, were in effect during World War II. The stockpile program, beginning in 1951, greatly stimulated domestic and free world production. Defense Minerals Exploration Administration assistance served as an incentive for exploring new deposits and in finding additional ore in known deposits.

During wartime shortages, tungsten was allocated to the most critical and essential uses.

PRICES

Figure 2 shows prices and corresponding domestic mine shipments for the years 1925–63. Although domestic prices under the Government purchase program exceeded $60 per short ton unit of WO_3 throughout the 1951–56 period, peak production was not reached until 1955.

TAXES

A 23-percent domestic and a 15-percent foreign depletion allowance is applicable to tungsten mines.

RESEARCH

Government agencies, private research organizations, and industry intensified the research effort on tungsten in the 1950–63 period. The effort was stimulated primarily by the increasing need for materials capable of withstanding extremely high-temperature environments.

Much of the research was basic in nature and included studies of structure, mechanical properties, oxidation mechanisms, thermodynamic properties, and phase equilibria. Preparation of extremely pure tungsten, research on analytical methods for determining impurities in minute quantities, and studies of the effects of impurity elements were also studied by numerous organizations.

Difficulty in fabrication arising from high, hot strength and room temperature brittleness has comprised one of the major obstacles to the wider use of tungsten. Melting and casting, metalworking, and alloy development comprised an important area of research aimed at improved fabricability, better oxidation resistance (above 2,000° F), or other special properties. Development of protective coatings for high-temperature applications was also an important objective.

Notable improvements were made in the techniques of powder metallurgy, especially in the production of larger size ingots and in the production of intricate shapes.

Other developments in tungsten fabrication include spinning, vapor deposition, flame plating, and explosive and high-energy rate forming (H.E.R.F.).

The Bureau of Mines tungsten program before 1957 was devoted largely to resources and extraction studies. In 1957, emphasis was shifted to research on analytical methods and preparation of ultrapure tungsten, and the Bureau investigated methods of obtaining tungsten metal by electrolytic and bomb-reduction techniques (*3–8*, *14*). Various radiotracer, fluorescent, and spectrographic methods were developed to analyze high-purity tungsten metal (*1–2*, *9*, *16*). Thermodynamic studies were conducted by Bureau scientists to obtain basic properties of tungsten compounds. Tungsten research was continued on vapor deposition and preparation of thick coatings (*10*, *13*). In a continuing search for new tungsten resources, Western deposits and reserves were investigated and evaluated in Montana, Arizona, Utah, and Colorado by Bureau geologists and mining engineers.

Continued tungsten research is being conducted at Bureau research centers. Metallurgists of the Albany Metallurgy Research Center, Albany, Oreg., are conducting investigations on the physical and extractive metallurgy of tungsten. At the Reno Metallurgy Research Center, studies of fused-salt extractive techniques are being conducted. Studies on the vapor deposition of tungsten are being continued at the Rolla Metallurgy Research Center, Rolla, Mo. Tungsten electroplating studies are being conducted at the College Park Metallurgy Research Center, College Park, Md. Additional tungsten research is being conducted or sponsored by the National Aeronautics and Space Administration (NASA), the Atomic Energy Commission (AEC), and by the Department of Defense (Navy and Air Force).

OUTLOOK

Because of tungsten's applications in the tools of production and its excellent high-temperature strength properties which are important in the growing nuclear and space industries, demand for it should increase. The tungsten mines of California and Colorado will continue to produce about 5.5 to 7 million pounds of tungsten annually if prices continue at the 1963 level. It is unlikely that any additional large mines will open at these prices unless lower cost mining and/or beneficiation processes are developed or cheaper and more efficient ways are developed to extract and process tungsten from low-grade ores.

Comparatively significant increases in tungsten consumption could result from the development of new applications for coated tungsten and its alloys having excellent high-temperature properties. Tungsten carbides are expected to continue to account for about 40 to 45 percent of the tungsten market since they are important constituents of modern tools and weapons. A short-term demand for tungsten is expected to arise from the research being conducted for the aircraft and space effort. Long-term demands are expected to depend on developing industrial applications which will utilize the high-temperature properties of tungsten in sheet and fabricated forms. Applications such as the direct use of nuclear heat to raise the temperature of process reactants probably will utilize the exceptional high-temperature strength of tungsten and its alloys. Because of its combination of high-temperature strength and resistance to penetration by subatomic particles, tungsten metal may be used in shielding applications. Other potential uses of tungsten are in structural components of fast nuclear reactors, aircraft engines, missiles, and space vehicles. Tungsten will find increasing application in the rocket-motor and rocket-nozzle fields. Because no other metal surpasses its high melting point and high-temperature strength, tungsten, when made oxidation resistant by the application of a suitable coating, is assured of an important place in future high-temperature metallurgy.

Although the U.S. tungsten ore resource of 140 million pounds represents about a 13-year supply, based on the 1963 consumption of 11 million pounds, domestic tungsten requirements are expected to increase to about 25 million pounds annually by 1980. This projected annual consumption, based on the projected growth of tungsten consumed in the steel, carbide, automobile, and aerospace industries, is almost one-fifth of the total measured, indicated, and inferred tungsten resources of the United States. Consequently, the presently known tungsten resource base will be inadequate to support any significant expansion in the years after 1980. The development of methods to recover tungsten from the brines of Searles Lake, Calif., could provide the required resource base to support the anticipated expansion after 1980.

During the past few years the world tungsten market has been disrupted by the abundant supply of tungsten which has been sold well below the market price. This material is believed to have originated primarily from mainland China and to have been shipped through the U.S.S.R. In the latter part of 1963 when a political rift developed between these two countries the supply of tungsten from China decreased significantly and world price steadily increased. The outlook for world supply of tungsten is one of surplus with possible continued disruption of world marketing channels by mainland China and U.S.S.R.

PROBLEMS

Although tungsten has excellent high-temperature properties, it, like the other refractory metals, oxidizes excessively at temperatures above 1,000° C. Currently the most urgent tungsten problem is the need to develop an oxidation-resistant coating or surfacing to protect tungsten and its alloys so that their high-temperature properties can be utilized. Tungsten alloys that are presently available have sufficient high-temperature properties to warrant their immediate application in missiles and rocketry, but these applications will be limited until the problem of oxidation resistance is overcome. Until adequate protective coatings are developed, the use of tungsten at high temperatures will be limited to short-term exposures, as in rocket nozzles, and to nonoxidizing environments.

Tungsten metal lacks ductility at room temperatures and consequently must be fabricated in nonoxidizing or inert atmospheres at elevated temperatures. Overcoming the problem of tungsten fabrication requires expensive and often complex equipment. Tungsten is ductile at room temperature if it is alloyed with rhenium. The resulting alloy has both good ele-

vated temperature properties and room temperature ductility. Rhenium, however, is expensive, $600 per pound, and in relatively short supply. To overcome the inherent disadvantages of rhenium, other metals are being considered for use as an alloying material with tungsten in an attempt to lower the ductile-brittle transformation temperature and obtain room-temperature ductility. One of the metals under consideration for this purpose is technetium, a sister element to rhenium, which can be obtained from the waste-fission products of nuclear reactors. This potentially large source of supply is in turn dependent upon the existence of waste-isotope separation facilities.

Resource problems revolve about knowing and defining the tungsten resource base. Some fundamental problems are associated with methods of exploring, appraising, and sampling. More complete and detailed information is needed on tungsten resources which are not currently considered commercial. Sufficient tungsten resources required for the long-term needs of the country have not been outlined. Measured, indicated, and inferred domestic tungsten ore resources constitute about 13-year supply at the present rate of consumption and only about 5-year supply at the demand rate expected in 1980. Much of this material is currently considered economic only at prices two to three times greater than present quotations. Incomplete knowledge of both domestic and free world tungsten resources and requirements indicates that more extensive exploration work should be conducted to adequately determine the reserves and resources.

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URANIUM

By Charles T. Baroch [1]

URANIUM is the primary nuclear fuel which, with thorium, forms the only fresh energy source developed this century. Reserves and resources are sufficient to supply the world's long-range energy demand for many generations as gas, oil, and coal resources become depleted.

Uranium is a fairly rare element comprising about 0.0002 percent of the earth's crust. It never occurs uncombined in nature. More than 150 minerals have been identified, but the chief ones are pitchblende and coffinite (primary) and carnotite (secondary). The major world sources are the Western United States, the Elliot Lake and Beaverlodge areas in Canada, Republic of South Africa, France, Australia, and several areas in Communist countries. Natural uranium consists principally of two isotopes. It is about 99.3 percent U^{238} and 0.7 percent of the fissionable isotope U^{235}.

When sufficient quantities of U^{235} or Pu^{239} are brought together in a properly shaped mass, a chain reaction occurs, releasing a vast store of energy which is actually derived from the conversion of matter to heat energy. Such a reaction, if uncontrolled, produces a violent explosion—the atom bomb. However, the flow of neutrons can be controlled at the proper rate to release this energy for the production of heat and power. It is unquestionable that the greatest contribution uranium will make in the future will be in creating useful power.

As soon as the military potential of uranium became known, practically every country in the world established controls over the production, transfer, or delivery of uranium and thorium materials. The first domestic controls were assumed by the War Department which established the Manhattan Engineer District in 1942. In 1946, control passed to a civilian agency, the U.S. Atomic Energy Commission (AEC) (*10*).[2] The Nation's first problem was a source of uranium supply. To supplement the meager supply available from the then known Colorado Plateau deposits, material was obtained from the Belgian Congo and Northern Canada. Additional early dependence for a substantial supply was placed on the uranium-bearing gold ores of South Africa, discoveries in Ontario, and smaller sources from Portugal and Australia. The Belgian Congo, Portuguese, and Australian contracts have been completed, all the South African contracts terminate on or before December 31, 1966, and the Canadian contracts have been modified to extend deliveries to the end of 1966. In the meantime deposits in the Western United States have been developed so that domestic production is adequate to supply present and near-future domestic requirements.

Initially, AEC contracted to purchase concentrates from several small mills which were reopened near Uravan, Colo. Later AEC opened its own mill at Monticello, Utah. As more ore discoveries were made, AEC made additional contracts with mills to produce specification-grade concentrates. Over 1,000 mines were producing ore by 1961, and developed reserves exceeded all expectations; more than enough uranium became available for any foreseeable military emergency. Consequently, production was cut back beginning in 1963 when uranium producers were invited to submit proposals for deferral to 1967 and 1968 of a portion of the concentrates originally contracted for delivery through 1966. An additional quantity of concentrates, equal to the amount deferred, will be purchased by AEC during 1969 and 1970.

As civilian uses of nuclear energy increased and as experience was gained in regulating those uses, AEC began to review the legal requirement for Government ownership of special nuclear material. The Atomic Energy Act was amended in 1964 to state that by June 30, 1973, all nuclear materials for civilian use, must be owned outright by private organizations. The amended act will lead to a competitive industry with prices for nuclear material based on fuel value rather than on weapon value. A transition period was provided for.

[1] Commodity specialist.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

As military requirements for uranium became assured, more attention was directed to peaceful uses of nuclear energy. The first extensive civilian and industrial application of nuclear forces was that of radioisotopes, which could be manufactured quite readily by irradiation of certain elements with neutrons or which were recoverable from fission products. Nuclear power reactors were more complicated and required more time and money to develop. By 1957, the first domestic commercial-sized nuclear power station started operation at Shippingport, Pa., with a capacity of 60,000 kilowatts. By the end of 1964, 13 central-station type plants having a capacity of more than 1 million kilowatts were operable, 5 others were under construction, and several more were under consideration. Also the nuclear-powered ship *Savannah* was sailing the high seas, as were 3 naval surface ships and 51 submarines.

The recovery of uranium from ore involves complicated and costly processing. Privately owned mills near the mines leach the ore with either acid or alkali carbonate, recovering the uranium from leach solution by direct precipitation, ion exchange, or solvent extraction methods and producing a concentrate known as yellow cake containing about 75 percent U_3O_8. Concentrates are refined by a nitric acid and solvent extraction process producing UO_3 which is then converted to uranium fluorides. Uranium tetrafluoride is reacted with magnesium to produce uranium metal, and the hexafluoride is sent to gaseous diffusion plants for enrichment in the U^{235} isotope. Metal is used in production reactors to produce plutonium, also a fissionable element used in weapons and fuel for other reactors.

Uranium concentrates from the mills are refined in plants owned by AEC but operated under contract by private firms. Three gaseous diffusion plants and two plutonium plants, also owned by AEC and largely a part of the weapons-production stream, are also operated by private firms under contract. Under the Atomic Energy Act of 1954 all source nuclear material had to be owned by the Government but could be made available to licensed users on a lease basis, but the law passed in 1964 will permit private ownership of nuclear materials.

As of July 1964, the known domestic ore reserve was about 160,000 tons of U_3O_8, and known free-world reserves totaled about 600,000 tons of U_3O_8.

The outlook for uranium is one of transition from a forced-draft subsidized military economy to a competitive market. The diminishing needs of the weapons program have left the future of the industry largely dependent on peaceful uses for uranium. Nuclear energy, a revolutionary source of new energy, is now developing into a competitive source of electricity. For the near term it will supplement rather than supplant the use of fossil fuel, and will provide a source of energy when fossil reserves are in short supply or become depleted. Some nuclear power plants now under construction are expected to be competitive in high cost fossil-fuel areas, and the AEC target growth curve indicates that nuclear power might supply as much as one-half of all electricity generated in the year 2000.

The next 20 years are expected to be transition years for the nuclear-power programs. New and improved reactor designs, accelerated rate of reactor construction, and improved reactor economics are expected. In 30 or 40 years breeder reactors are expected to become the principal source of nuclear power and, with their increase fuel economies, almost unlimited supplies of high-cost uranium and thorium should become economic.

AEC research will probably continue for some time in chemistry, metallurgy, and physics. Part of this research is conducted in its own laboratories operated by industrial concerns, and part is conducted by research grants to educational institutions.

Many problems confront all phases of the nuclear-power industry. A broad field for research lies in the operation and design of nuclear reactors and the search for a highly efficient type to reduce the cost of nuclear power. Both government and industry have made progress in solving many uncertainties, and many experimental power reactors are forming the base for the accumulation of knowledge and experience.

BACKGROUND

Uranium was discovered by H. M. Klaproth in 1789 in pitchblende and was named after the planet Uranus. In 1896, Henri Becquerel discovered radioactivity while studying the phenomena of phosphorescence and fluorescence. He noticed that uranium salts emitted an invisible radiation that was capable of traversing thin layers of opaque materials and affecting a photographic plate. He also discovered that the air near uranium salts was ionized; that is, it was electrically conducting so that a charged electroscope would be discharged.

In 1898, G. C. Schmidt and Madame Curie independently observed that similar radiations were emitted by thorium, and Madame Curie and her husband, Pierre Curie, discovered the

highly radioactive elements polonium and radium. Other radioactive elements were isolated, and in 1902, Ernest Rutherford and Frederick Soddy proposed the theory of radioactive disintegration. Scarcely noticed by the rest of the world, these tortuous years of physical research by a few geniuses opened up revolutionary concepts of matter and laid the foundation of the nuclear age.

Radium, one of the natural products from the radioactive decay of uranium 238, is strongly radioactive, and it soon found applications, principally in medicine for cancer therapy. In spite of its scarcity and its high price, a demand began to grow. The first radium was recovered from pitchblende from the Joachimsthal mine in Bohemia. In the search for additional uranium-radium sources attention finally centered on southwestern Colorado and southeastern Utah where carnotite was known. Colorado became a major producer of uranium ore for its radium content about 1911, and in 1912 about 1,200 tons of carnotite was shipped to France from which about 8 grams of radium was extracted. The Bureau of Mines and the National Radium Institute cooperated in mining and concentrating carnotite ore from 1914 to 1916. A radium recovery plant was built in Denver, and about 69,000 pounds of U_3O_8 and 8.8 grams of radium were recovered under this agreement. Then the plant passed into private hands. However, rich deposits were discovered in Katanga, Belgian Congo, and soon dominated the market; the domestic uranium industry collapsed around 1923.

The rich pitchblende deposits at Great Bear Lake, Canada, were discovered in 1930, and a refinery at Port Hope, Ontario, began extracting radium in 1933. From then until the early 1940's the uranium industry was divided between Canada and Belgium under a cartel agreement, and radium was the chief product sought. The uranium content had few uses, although a small amount was recovered for use as a coloring agent in ceramics and glass products and in photography. The market in these fields prior to World War II was about 200 tons per year.

In January 1939, when war clouds were first gathering in Europe, word was received that two German scientists, Otto Hahn and Fritz Strassman, had split the uranium atom. The experiment was repeated within a matter of days in a number of U.S. laboratories, and the scientific community became aware of the enormous amounts of energy that could theoretically be released in a chain reaction. After World War II started, the military possibilities of nuclear energy loomed importantly, and the interest in military uses was given a sense of urgency by the fear that Germany was experimenting in this direction.

On August 2, 1939, Albert Einstein signed a letter advising President Roosevelt of the possibilities of an atomic bomb, and the President soon after appointed an Advisory Committee on Uranium to examine the possibilities. In March 1940, it was conclusively demonstrated that uranium 235 could be fissioned. Three months later, the United States began a small integrated research program, and in August 1942, the Manhattan District, U.S. Army Corps of Engineers, was established to launch a full-scale research program on the atomic bomb, including the difficult problem of separating U^{235} from U^{238} (*10*).

On December 2, 1942, Enrico Fermi, with his small staff present, slowly withdrew the cadmium control rods that initiated the world's first self-sustaining chain reaction. This first reactor, designated as CP–1, was a makeshift pile without even a container jacket surrounding it, containing almost 400 tons of graphite, 6 tons of uranium metal, and 58 tons of uranium oxide, had been built in a converted game court at Stagg Field, University of Chicago. The reactor had operated only a few minutes with a release of less than a watt of energy, when the rising radioactivity required Fermi to shut down the reaction. However, the reaction was sufficient to initiate the so-called "atomic age," and the race for the bomb took tangible direction.

Procurement of uranium ore in sufficient quantities for large-scale production of fissionable materials began late in 1942. The Radium Chemical Co., Inc. of New York, had had sufficient foresight to import about 1,200 tons of high-grade pitchblende ore from the Belgian Congo in 1939 and 1940. It was intended as a wartime source of radium, but it assisted greatly with the work of the Manhattan District. In 1943, ore began to come by airlift from the rehabilitated Eldorado mine, by boat from the Congo, and as a byproduct of vanadium production at Naturita, Colo. Initially the Port Hope refinery was the only processor, but other plants were built in 1943 and 1944. The Combined Development Agency was created in 1944 by agreement between the United States and Great Britain to gain control of and to secure uranium and thorium supplies in certain areas of the world. Contracts were let to purchase uranium concentrates produced in the Belgian Congo, the Republic of South Africa, Australia, and Portugal. Deliveries on all these have been completed except those from South Africa which are to continue to the end of 1966.

Meanwhile an intensive effort to develop the atomic bomb continued in other fields. In 2½

years, the Manhattan District assisted by many giant American industrial concerns, built secret cities and plants, which included among others the billion-dollar Oak Ridge, Tenn., isotope-separation plant and laboratories; the $350 million Hanford, Wash., plutonium production plant; and the Los Alamos, N. Mex., Scientific Laboratory. The project ranks high as an engineering feat; yet, the most remarkable part was the fact that tens of thousands of people worked on the project, but probably not over 100 of them knew the full purpose of the work.

The purpose of nuclear developments up to 1945 was exclusively military, even though the peacetime possibilities of nuclear energy became apparent when the first chain reaction was confirmed. The Atomic Energy Commission was created by the Atomic Energy Act of 1946, and it was given the full burden of nuclear responsibilities formely held by the Army's Manhattan District. As an independent civilian agency of the Federal Government, it assumed direction of the development, use, and control of atomic energy for the defense and security of the United States and for peaceful applications. The Atomic Energy Act of 1954 permitted private persons to possess and use special nuclear materials under license, but required the mandatory government ownership of all nuclear materials. In effect, this invited the public to participate in the coming nuclear developments.

As late as 1946, domestic resources of uranium appeared to be negligible; only about 15 mines on the Colorado Plateau produced in that year. In 1948, AEC initiated a procurement program that provided guaranteed minimum prices for domestic ore, a bonus for the discovery and production of high-grade domestic ore, a mine-development allowance, premiums for higher-than-average grade ore, and allowances for haulage. Gold tailings from some of the mining operations in the Union of South Africa contained uranium, and arrangements were made to recover it. Production began in 1952. The 1948 program also was extended to Canada, leading to the discovery of significant deposits, and contracts for the purchase of Canadian uranium resulted.

The program's incentives produced results beyond expectation beginning with the finding of large deposits in the Colorado Plateau and Wyoming. One discovery led to another, and by 1954 over 900 mines produced uranium ore in the Western United States. In 1956 a new program provided for the purchase of concentrates at $8 per pound of U_3O_8 to begin after the ore-buying program expired on March 31, 1962. An announcement on November 24, 1958, limited the previous offer to uranium concentrates derived from reserves developed before November 24, 1958.

The peaceful uses of nuclear energy were designated by the act of 1946 as an important part of the AEC responsibility, and the development of reactors and radioisotopes proceeded on a large scale. The program spread worldwide through the International Atomic Energy Agency (IAEA), and later the European Atomic Energy Community (Euratom) was established by Belgium, France, West Germany, Italy, Luxembourg, and the Netherlands—all working under the slogan "Atoms for Peace." These programs led to the building of research, test, and training reactors all over the world, and the planning of various types of power reactors. In the United States the first large-scale power reactor, the Shippingport, Pa., Atomic Power Station, achieved full power in December 1957, and by the end of 1964, 13 power reactors with a rated capacity of more than 1 million kilowatt-hours were operable.

Uranium production caught up with the requirements, and a substantial military stockpile, so urgently needed at the start, showed signs of reaching fulfillment. Consequently, steps had to be taken to reduce the threat of overproduction. In November 1962, AEC announced that uranium mills could elect to defer to 1967 and 1968 a portion of the concentrates contracted for delivery by the end of 1966. In return for the stretchout, AEC would contract to receive during 1969 and 1970 an additional amount of concentrates, equal to the amount deferred beyond 1966, but at a price based on cost of production and not to exceed $6.70 per pound of U_3O_8.

AEC, although entitled by law to consider all things nuclear to be its monopoly, has pursued a consistent policy of liberalizing its regulations. Certain phases of regulatory authority have been delegated to those States that showed capability to control nuclear materials and which would enter into agreements with AEC regarding the same. In 1964, Congress passed Public Law 88–489 which amended the Atomic Energy Act of 1954 to permit private ownership of special nuclear materials and repealed the requirement of their mandatory Government ownership. Licensing will still be necessary, but after December 31, 1970, AEC will not be able to distribute special nuclear material except by sale.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

The uranium industry throughout the world has been developed under the direction of

the various governments. Demand has been founded almost entirely on military requirements. Prices were largely determined by military necessity and, in many cases, involved above-cost incentives or permitted accelerated amortization of development work to be calculated into costs. In free-world countries most of the production has been done by privately owned mines and mills licensed by a Government agency which has also been the purchaser. Roughly about 85 percent of free-world uranium produced through 1963 was purchased by the United States, and most of the balance went to the United Kingdom.

In the United States, the Atomic Energy Act of 1954 required Government ownership of all fissionable materials but provided for the encouragement of private development within vaguely defined boundaries of peaceful uses of nuclear energy. Procurement of domestic uranium concentrates was arranged through contracts with privately owned mills. The 20 mills operating at the end of 1964 are shown in table 1. The mills receive ore from company-owned mines or purchase it from independent operators. AEC has always required each mill to accept a certain portion of their capacity from custom shippers. Contracts with the mills control the rate of concentrate delivery and prescribe by allocation the amount of ore deliverable. Acceptable concentrates have to be produced from ore reserves developed prior to November 24, 1958.

TABLE 1.—*Uranium processing plants in the United States, Dec. 31, 1964*

State and company	Plant location	Date of first delivery to AEC	Capacity, tons per day
Arizona: El Paso Natural Gas Co	Tuba City	July 1956	300
Colorado:			
American Metal Climax, Inc	Grand Junction	June 1951	330
Cotter Corp	Canon City	Aug. 1958	200
Union Carbide Corp., Nuclear Division	Rifle	Dec. 1947	1,000
Do	Uravan	Mar. 1950	1,000
New Mexico:			
The Anaconda Co	Grants	Sept. 1953	3,000
Homestake-Sapin Partners	do	Sept. 1958	3,000
Kermac Nuclear Fuels Corp	do	Dec. 1958	3,300
Vanadium Corp. of America	Shiprock	[1] Jan. 1955	300
South Dakota: Mines Development, Inc	Edgemont	Aug. 1956	400
Texas: Susquehanna-Western Corp	Falls City	June 1961	200
Utah:			
Atlas Corp	Moab	Nov. 1956	1,500
Do	Mexican Hat	[1] Nov. 1957	1,000
Vitro Chemical Co	Salt Lake City	Oct. 1951	600
Washington: Dawn Mining Co	Ford	Sept. 1957	400
Wyoming:			
Federal-Radorock-Gas Hills Partners	Fremont County	Dec. 1959	520
Globe Mining Co	Natrona County	Feb. 1960	490
Petrotomics Co	Carbon County	Apr. 1962	200
Utah Constructions & Mining Co	Fremont County	Mar. 1958	980
Western Nuclear, Inc	Jeffrey City	Aug. 1957	850

[1] First delivery from plant by previous owner.

As many as 1,000 mines have been in production in any one year, and in 1963, 730 mines in 14 States provided about 5.9 million tons of ore. Individual mines vary in size from small "gopher holes" that produce only a few tons to those that have produced in excess of 200,000 tons annually. In 1963, about 400 mines individually produced over 1,200 tons of which about 90 produced over 12,000 tons.

Uranium concentrates are shipped to the AEC refinery at Weldon Spring, Mo., which is operated by Mallinckrodt Chemical Works and produces UO_3, UF_4, and high-purity natural uranium metal. Production reactor fuel cores are fabricated in an AEC plant at Fernald, Ohio, operated by National Lead Co. of Ohio. About 600 people are employed at Weldon Spring and 1,750 at Fernald. UO_3 is processed to UF_6 at the AEC plant at Puducah, Ky., which is used there as feed to a gaseous diffusion plant. The product is then sent to AEC gaseous diffusion plants at Oak Ridge, Tenn., and Portsmouth, Ohio, for further enrichment. The Paducah and Oak Ridge plants are operated for AEC by Union Carbide Corp., and the Portsmouth plant is operated by Goodyear Atomic Corp. These plants represent investments of about $785 million, $850 million, and $770 million, respectively, and during peak op-

erations employed about 1,800; 6,000; and 2,700 people.

Private industry has gradually developed a capability for producing uranium materials and fabricating nuclear fuels, and about the only remaining major area in the fuel cycle still performed solely by the Government is gaseous-diffusion uranium enrichment. Principal producers of uranium materials and fabricators of uranium fuels are listed in table 2.

Plutonium is produced in nine graphite-moderated production reactors at Hanford, Wash., which have been operated by General Electric Co., and which is withdrawing from the operation in 1965. Battelle Memorial Institute was selected to operate the laboratories. Five heavy-water production reactors at Savannah River, S.C., operated for AEC by E. I. du Pont de Nemours & Co., Inc., also produce plutonium.

Early in 1964, President Johnson announced a cutback in nuclear weapons production beginning July 1, 1965, and spread over approximately 3 years. The feed plant at Paducah was closed June 30, 1964, and three production reactors at Hanford were to be shut down, one January 1, 1965, and the other two at 3-month intervals after that. One reactor at Savannah River was shut down in July 1964.

TABLE 2.—*Principal producers of uranium materials and fabricators of uranium fuels*

Company and principal location	Metal, oxides, and compounds	Coated particles	Fabricators of uranium fuels
Aeroject General Nucleonics, San Ramon, Calif			×
Allis-Chalmers Manufacturing Co., Greendale, Wis			×
Atomics International, Canoga Park, Calif			×
The Babcock & Wilcox Co., Lynchburg, Va			×
Battelle Memorial Institute, Columbus, Ohio [1]			×
The Carborundum Co., Niagara Falls, N.Y.[1]			×
Combustion Engineering, Windsor, Conn			×
Coors Porcelain Co., Golden, Colo			×
Diamond Alkali Co., Painesville, Ohio		×	
General Electric Co., San Jose, Calif.[1]	×		×
General Dynamics Corp., San Diego, Calif		×	×
Kerr-McGee Oil Industries, Inc., Cushing, Okla	×		
Martin Marietta Corp., Baltimore, Md			×
Metals & Controls Inc., Attleboro, Mass			×
Minnesota Mining & Manufacturing Co., St. Paul, Minn		×	
National Carbon Co., Lawrenceburg, Tenn		×	
National Lead Co., Albany, N.Y	×		×
Nuclear Fuels Services, Inc., Erwin, Tenn	×	×	×
Nuclear Materials & Equipment Corp., Apollo, Pa.[1]	×	×	×
Nuclear Metals Inc., Concord, Mass			×
Sylvania Electric Products, Inc., Hicksville, N.Y			×
United Nuclear Corp., Hematite, Mo.[1]	×	×	×
United Nuclear Corp., New Haven, Conn			×
Westinghouse Electric Corp., Pittsburgh, Pa			×

[1] Also possess some capabilities for processing plutonium.

Source: Adapted from AEC Annual Report for 1964.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS (11)

Uranium, chemical symbol U and atomic number 92, is the last member of the series of naturally occurring elements in the Periodic Table. Natural uranium contains the three isotopes U^{238} (99.285 percent), U^{235} (0.71 percent), and U^{234} (0.0051 percent).

U^{235} is the only naturally occurring, fissionable nuclide, and its content in natural uranium varies only slightly, from about 0.7103 to about 0.7113 percent by weight, depending on its geographical source. Effective July 1, 1963, the accepted value of 0.711 was established by AEC unless an actual measured U^{235} value was determined. U^{235} is not a member of either the uranium-radium or thorium disintegration series, and its origin in natural uranium is a matter of deep speculation.

U^{238} is the most common natural isotope and is of great importance because it is one of the two fertile materials available for producing fissionable material. U^{238} yields plutonium 239, Pu^{239}, under neutron bombardment.

U^{234} is a nonfissionable, long-lived isotope of no practical importance as a nuclear material as it is not fertile.

All uranium isotopes are naturally radioactive, and the half-lives of U^{235} and U^{238} are

7.1×10^8 and 4.51×10^9 years, respectively. Because of the slow rate of radioactive decomposition, recently prepared pure uranium is only mildly radioactive. Freshly mined ores that are in equilibrium with their daughter products, are radioactive largely because of the presence of short-lived and intensely radioactive elements, such as thorium 234, radon 222, polonium 218, and others. U^{238} decays in accordance with the uranium-radium series and leads to a stable lead isotope, Pb^{206}. U^{235} decays through the actinium series, producing also a stable lead isotope, Pb^{207}.

A number of uranium isotopes can be produced artificially. U^{233} is an important fissionable material that is formed by the neutron bombardment of thorium 232. It has the highest neutron yield in thermal fission and offers great promise as a power source in breeder reactors. U^{236} is formed to a slight extent in reactors by irradiation of U^{235}. Like U^{234} it has no use as a fuel and serves only to complicate the reprocessing of nuclear fuel. U^{237} is a short-lived isotope (6.8 days) and decays to Np^{237} which is a source material for Pu^{238}, a good heat source for special applications.

Uranium has a density of 18.7, nearly that of gold and 65 percent heavier than lead. It is reasonably ductile and can be fabricated by usual metal-working methods. It has poor structural strength and is generally regarded as being semiplastic. It is highly reactive chemically, and a freshly cut surface of silvery gray rapidly oxidizes to black oxide in air at room temperature. Chips and powder are highly pyrophoric, and the metal is a strong reducing agent reacting with all nonmetallic elements. The normal valences of uranium are +3, +4, and +6, and four oxides, UO, UO_2, U_3O_8, and UO_3 are known, but pure UO has been definitely established only as a thin surface layer on the metal.

U_3O_8, a uranium-uranyl oxide, is olive-green in color and contains 84.8 percent uranium. Most chemical analyses for uranium are expressed in terms of U_3O_8 and ore purchases are made on that basis.

UO_2, or *brown oxide*, is commonly used for fabricating fuel elements for power reactors and is also an intermediate product in producing uranium tetrafluoride from UO_3.

UO_3, or *orange oxide*, is produced at one stage of the refining process.

Yellow cake is the term applied to certain uranium concentrates produced by mills. It is the final precipitate formed in the milling process, and it is usually considered to be ammonium diuranate, $(NH_4)_2U_2O_7$ or sodium diuranate, $Na_2U_2O_7$, but the exact composition is variable and depends upon the precipitating conditions.

AEC has established specifications for uranium concentrate delivered under its contracts. All concentrate shall pass through a 0.25-inch screen and shall be amenable to refining by solvent extraction as determined by standard tests. Price penalties are provided for concentrates containing less than 75.00 percent U_3O_8 and for specific impurities exceeding the following maximum allowable quantities expressed as a percentage of the contained U_3O_8, except in the case of the last two items:

Constituent:	*Percent*
Vanadium oxide, V_2O_5	2.00
Phosphate, PO_4	4.00
Molybdenum, Mo	.60
Boron, B	.20
Halogens, Cl, Br, and I, expressed as Cl	.30
Fluorine, F	.10
Arsenic, As	2.00
Carbonate, CO_3	4.00
Sulfur as SO_4	10.00
Calcium, Ca	1.50
Thorium, Th	2.00
Zirconium, Zr	2.00
Samarium, Sm	.015
Europium, Eu	.015
Gadolinium, Gd	.015
Dysprosium, Dy	.015
U_3O_8 insoluble in nitric acid [1]	.10
Organic content [1 2]	.10
Moisture, H_2O [3]	10.00

[1] As determined by the standard method used by AEC for making such determinations.
[2] Concentrate shall be free of surface-active organic materials, which are found by AEC to interfere with subsequent refining of the concentrate by solvent extraction.
[3] Determined on an "as received" basis and drying at 110° C.

Fission and Nuclear Energy

Fission, when applied to nuclear phenomena, is the transmutation process whereby a fissionable element is divided into two other elements. Fission occurs when an atomic nucleus is hit by a free neutron which has the proper amount of energy (speed) to be captured (or incorporated) into the nucleus. The nucleus responds by flying apart violently, forming two new elements, known as *fission fragments*, which range in mass from 72 to about 160. The combined mass of the fission products is less than the mass of the original atom. The difference represents matter that has been converted into heat energy in accordance with Einstein's law.

Nuclear energy, often called *atomic energy*, is energy derived from fission. Albert Einstein stated the relationship between mass and energy which is fundamental to the whole subject of nuclear energy. This equation shows that the relationship between energy (E) and mass (m) is $E=mc^2$, where c is the velocity of light. Since the velocity of light is large (nearly 3×10^{10} centimeters per second), a small mass is equivalent to a very large quantity of energy.

One gram of matter is equivalent to 25 million kilowatt-hours of energy. In the fission of uranium only about 0.1 percent of its mass is converted into energy, and the fission of all the atoms in a gram of U^{235} will yield about 23,000 kilowatt-hours or about 1,000 kilowatt-days of energy. Conversely, 1,000 kilowatt-days of energy equals the fission of 2.70×10^{21} atoms. Thus, 1 gram of U^{235} burned in a nuclear way will release as much heat as 3 tons of good quality coal. One pound of fissionable matter will yield 0.999 pound of fission products, and the 0.001 pound of mass is converted into the heat equivalent of over 10 million kilowatt-hours of energy.

In addition to the fission products and energy produced by fission, an average of about 2.5 high-energy neutrons are also released. This is one of the most notable features of nuclear fission, and the one that makes nuclear energy possible. These released neutrons have the capability of causing additional fission to continue in a process known as a *chain reaction*. Under certain conditions, a chain reaction can proceed rapidly and result in an enormous explosion, such as that produced by nuclear or atomic bombs. On the other hand, the reaction can be controlled by neutron-absorbing materials and neutron moderators, so that fissioning takes place at a selected rate.

A nuclear reactor is an assembly of nuclear fuel, control devices, coolant, and containment vessels capable of sustaining a chain reaction at a desired rate. *Power reactors* are used as an energy source for electric-power production, space heating, or for propulsion. *Production reactors* are used to produce plutonium 239 for defense stockpiles. *Research*, *test*, and *training reactors* are used to provide intense beams of fluxes of neutrons for experimental purposes or for producing radioisotopes.

Fertile materials are uranium 238 and thorium 232 which can be transmuted by the capture of neutrons into fissionable plutonium 239 and uranium 233, respectively. Fertile materials are frequently incorporated into the fuels of nuclear reactors, and reactors can be designed to operate on *natural uranium*, which contains essentially 0.71 percent U^{235} and 99.285 percent U^{238}. *Depleted uranium* is uranium from which the fissionable isotope, U^{235}, has been partially or completely separated. It can refer to any U^{239} containing less than 0.7 percent U^{235}.

An *isotope* or *nuclide* is a variant form of a given chemical element due to differences in the number of neutrons contained in their nuclei. Isotopes of the same element have the same number of protons in their nuclei and the same electron arrangement, hence they are practically identical in chemical behavior but differ in atomic mass.

A radioactive isotope is called a *radioisotope* or *radionuclide*. A few radioisotopes are found in nature, but many more can be made in nuclear reactors by bombarding elements with neutrons. Typically, natural and stable cobalt 59 can be converted into cobalt 60 which emits gamma rays, similar to X-rays, and is used for medical teletherapy and industrial radiography. *Fission fragments* or *fission products* resulting from the fission of heavy nuclei are a mixture of about 35 elements and may contain nearly 200 different stable and radioactive isotopes. Fission products are possible sources of high-intensity radiation for various industrial applications.

Neutrons are uncharged or *neutral* particles which, with *positively charged protons*, make up the *nucleus*, the dense, positively charged core of all atoms heavier than the hydrogen atom. An atom is similar to a tiny solar system with a nucleus surrounded by orbiting *electrons*. Electrons are elementary particles carrying a *negative* charge and having a mass when at rest equal to $\frac{1}{1838}$ that of the hydrogen atom, which consists of one proton and one electron. Neutrons have approximately the same mass as protons, therefore, the bulk portion of an atom is the nucleus. Nuclei of different elements are made up of different numbers of neutrons and protons and, when electrically neutral, the atom has the same number of electrons as it has protons. For instance, U^{235}, which is one of the largest and most complex of the naturally occurring elements, has a nucleus of 143 neutrons and 92 protons, totaling 235 mass units, around which 92 electrons are orbiting.

Fusion, or *thermonuclear fusion*, occurs when nuclei of lightweight elements combine to form heavier nuclei. In many respects the fusion process is just the opposite of fission. However, a large amount of energy is released in the fusion process, which is also the result of transformation of mass into energy. Fusion is the basis of the hydrogen bomb and depends on the fusion of either two deuterium nuclei or of a deuterium nucleus with a tritium nucleus to form helium 4. Deuterium and tritium are isotopes of hydrogen. Deuterium occurs naturally in the ratio of 1 part in 6,000 of hydrogen, and the ocean contains enough deuterium to provide power requirements at the present rate of use for many hundreds of millions of years. A great number of formidable problems must be solved before fusion power can become a reality.

Radiation Hazards

Atomic energy is unique compared with other energy sources because of its radioactivity, which is associated with the entire nuclear program from the uranium minerals in the earth to the end product of its use. Radioactive materials emit energy that can damage living tissue. The major forms of radiation are alpha particles, beta particles, gamma rays, and neutrons (radiation is described in the Radium chapter). Some elements such as uranium, thorium, and radium, are naturally radioactive, while others become radioactive after bombardment with neutrons. Many radioactive isotopes are produced by placing material in a nuclear reactor and bombarding it with neutrons.

Potential danger of exposure to radiation has become a major concern to the public. Military and civilian atomic energy use, along with the great increase in production and processing uranium ores, introduced new sources of radioactive materials into man's environment. New problems requiring thorough study and careful long-range planning have been created.

Uranium miners are exposed to alpha, beta, and gamma radiation. The hazards exist as external sources and as radioactive gas (radon) and particulates which can be inhaled and retained in the body. Radiation studies in uranium mines show that the greatest hazard to the miners is produced by radon decay products (daughters). Radon is a highly radioactive gas derived from the disintegration of radium. It has a half life of 3.825 days and disintegrates successively into various radium isotopes, finally ending as stable Pb 206. Practically all mines require mechanical ventilation to reduce the atmospheric concentrations of radon and its daughters to the working levels recommended by the Public Health Service and other agencies.

Radium A and Radium C′, the two alpha-emitting isotopes of the daughter products, are the principal direct sources of excessive radiation dosage. Studies by the Public Health Service have shown that a serious health hazard exists from ingestion of radon daughter products that might cause lung cancer if continued over a number of years. A tolerance level for radon daughter product concentrations of 300 micromicrocuries per liter of air was recommended in 1955 at a joint conference of government agencies and mine operators. Studies and research by government and State agencies are continuing toward control and attenuation of the hazard.

Uranium mills employing modern wet processes usually have no serious difficulty in maintaining safe working levels of radioactivity for employees. The major problem of the mills is the disposal of effluent liquors and tailings that may contaminate surface and underground water resources. The principal source of contamination is the radium content remaining in the tailings. The radium is slowly water-soluble and may become a contaminant.

External radiation presents only minor problems in mines and mills because both uranium ore and concentrate emit only low-level radiation which is not considered dangerous under normal working conditions.

Development of atomic energy has brought about radiation intensities far greater than anything that had been previously experienced. Radiation from the fission of uranium, spent uranium fuel elements, and radioisotopes, among others, must be attenuated to protect personnel. Attenuation by shielding and other means increases the costs of atomic energy. In addition, the hazards of reactor operation present civil as well as technical problems. Localities, States, and governments are concerned about potential hazards of atomic energy, including those associated with disposal of radioactive wastes and radioactive fallout produced by the detonation of nuclear weapons. Regulations on standards for protection against radiation were issued by the AEC in January 1957. The rules establish standards for protection of atomic energy workers and the public against radiation hazards arising from activities licensed by the Commission (*1*).

TECHNOLOGY

Geology (*9*)

Geochemists estimate that uranium makes up about 1 to 2 parts per million of the earth's crust, greater than that of antimony, bismuth, mercury, silver, and gold and about the same as that of cobalt, lead, and molybdenum. Many primary igneous rocks, particularly the granites, contain uranium in concentrations rarely as high as 50 parts per million. Such rocks existing in past geologic ages are considered to be the sources of many of the higher grade concentrations now being exploited, particularly those found in sedimentary rocks.

Uraninite, the most common uranium mineral, ideally is UO_2, but usually contains UO_3. The massive form is called pitchblende. As a primary mineral it is found in small amounts throughout the world, often concentrated in pegmatites and primary vein deposits. It is also found in secondary deposits.

Coffinite, a uranium silicate, is a major uranium mineral in the unoxidized ores of the Western States.

Carnotite, $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot nH_2O$, is the

most important secondary uranium ore mineral. Probably another 150 secondary uranium minerals have been identified and are found in small concentrations, many of them being complex hydrated compounds of uranium, copper, lead, vanadium, molybdenum, iron, magnesium, calcium, potassium, and sodium oxides or phosphates. The more common secondary minerals in addition to carnotite are—Tyuyamunite, $CaO \cdot 2UO_3 \cdot V_2O_5 \cdot nH_2O$; autunite, $CaO \cdot 2UO_3 \cdot P_2O_5 \cdot nH_2O$; uranophane, $CaO \cdot 2UO_3 \cdot 2SiO_2 \cdot 6H_2O$; torbernite, $CuO \cdot 2UO_3 \cdot P_2O_5 \cdot nH_2O$; and gummite, $UO_3 \cdot nH_2O$ containing also various quantities of other elements. Combinations of these minerals often form spectacular displays of color. In many carnotite deposits, the uranium is intimately associated with carbonized wood or other carbonaceous matter, which are good indicator substances to the prospector.

Uranium is also found as a minor constituent of many minerals which are multiple complex oxides, such as thorianite (uranothorianite), $(ThU)O_2$; and the fergusonite-formanite, samarskite-yttrotantalite, and euxenite-polycrase series of minerals, which are made up of rare-earth oxides and either or both columbium or tantalum. Quadrivalent uranium is isomorphous with thorium, zirconium, and the rare-earth elements, and may be found associated with minerals of these elements.

Probably no other metal has ever received such concentrated mineralogical and geological study as uranium received from 1946 to 1960. Practically all occurrences were included in the studies, and the literature is very extensive.

The chief sources of ore in the United States are found in sedimentary strata, consisting of sandstone, mudstone, and limestone in which the uranium minerals occur as pore fillings, replacements of woody tissue or other carbonaceous matter, or as cement between quartz grains or along fractures. Several theories have been advanced to account for the origin of these deposits. They were formed later than the enclosed rocks, and evidently the primary ores, uraninite and coffinite, were deposited in carbonaeous sandstones under reducing conditions. Lowered ground water level permitted oxidation, changing uranium from the quadrivalent to the hexavalent form.

The largest and most numerous sedimentary uranium deposits are found on the Colorado Plateau, an area embracing about 150,000 square miles of western Colorado, eastern Utah, northeastern Arizona, and northwestern New Mexico. The uranium deposits occur as bedded bodies chiefly in the Morrison formation of Jurassic age and the Chinle conglomerate and Shinarump formation of Triassic age. In Wyoming, extensive uranium deposits occur mainly in sediments of Tertiary age. Other smaller deposits are found in Mesozoic, Paleozoic, and Tertiary sediments on the fringes of the Plateau and in California, Montana, Neveda, North Dakota, South Dakota, and Texas.

Uranium ore bodies in sedimentary rocks are spotty in distribution and vary from a few inches to several feet in thickness and up to several thousand feet in length. They are usually irregular in shape and most are tabular, paralleling the bedding, but some form lens-shaped bodies. Uranium content of most ore bodies ranges from 0.10 to 0.50 percent U_3O_8, with much higher grade local enrichments, and many contain vanadium.

Very few deposits similar to the sedimentary deposits of the Western United States are known elsewhere, and these are notably in Argentina and the U.S.S.R.

Some of the world's richest and most productive uranium deposits have been found in vein deposits. Pitchblende, associated with gold, silver, and base-metal sulfides or with fluorite, is the principal uranium mineral at depth. Uranium is mined in the United States from veins principally in Washington, Arizona, Utah, and Colorado, and to a lesser extent from veins in Oregon, Nevada, California, New Mexico, Montana, and Idaho.

Uranium vein deposits in Canada include the famous Eldorado mine in the Great Bear Lake area, Northwest Territories and the Goldfields Region in Saskatchewan. In Europe, vein deposits are found in Joachimsthal, Bohemia, and the Erzgebirge district which extends into East Germany; in Saxony; the Black Forest, Germany; and the Brittany Massif, Massif Central, and Vosges, France. The principal uranium deposits in Portugal are veins in coarse-grained granite, of which the Urgeirica mine is the most famous and dates from 1911, when it started as a producer of radium. The Shinkolobwe mine in Katanga, Congo (Leopoldville), began producing radium in 1921 and was unrivaled until the Eldorado mine began production in 1933. The Shinkolobwe mine closed down in 1960, its ore exhausted. Australian vein deposits are found at Rum Jungle in the Darwin-Katherine area.

In the Republic of South Africa, the Witwatersrand deposits are the important sources of uranium. Gold ores occur in about a dozen thin conglomerate beds called "reefs," some of which contain an average of nearly 0.5 pound of U_3O_8 per ton. A few bodies that could not be mined profitably for gold alone, contain about 1.25 pounds of U_3O_8 per ton.

Few replacement uranium deposits are known, but exceptions are the uranothoranite deposits in the Bancroft region, Ontario, and the Man-

dare River basin in the Malagasy Republic, as well as the Mary Kathleen pitchblende deposit in Queensland, Australia.

In the Blind River district north of Lake Huron, in Ontario, uranium occurs in Precambrian pyritic conglomerate beds containing disseminated grains of uraninite and brannerite. Some thorium is associated with the uraninite, together with cobalt and tungsten.

Many radioactive mineral occurrences in the United States have been found in pegmatites; however, few have produced significant quantities of ore. Typical deposits that have been economic sources of uranium lie in the Malagasy Republic, the Evje district in Norway, the Bancroft district in Ontario, and several occurrences in South Dakota and Colorado.

Nearly all igneous rocks contain trace amounts of uranium and thorium, and no nation need be deprived of either of these elements—at a price. The silicic and alkali silicic rocks contain the most uranium, and one of the highest grade large deposits is the Conway granite, outcropping over 300 square miles of area in New Hampshire, which averages about 12 parts per million uranium and 50 parts per million thorium.

Uraniferous black shales containing 0.001 to 0.006 percent U occur in many States, often covering large areas. The Chattanooga shale covers about 40,000 square miles across central Tennessee and into Kentucky and Alabama. It is generally less than 35 feet thick and the favorable uraniferous member averages about 0.006 percent U, and will yield up to 15 gallons of shale oil per ton. Other shales are found in Illinois, Kansas-Missouri-Oklahoma, Wyoming-Nebraska, North Dakota, and Montana, and deposits are known in Norway and the U.S.S.R. These deposits are low in grade and will serve only as resources for the distant future. Some higher grade shale in Sweden is being processed for uranium.

Many western lignites contain small amounts of uranium. Some of the largest deposits are in western North Dakota and South Dakota, extending into Montana, ranging from 0.01 to 0.20 percent U_3O_8. After burning, the ash from some of the higher grade lignites contains up to 0.50 percent U_3O_8, and 0.20 to 0.40 percent molybdenum, both of which have been recovered profitably. Other deposits are found in Wyoming, Utah, Nevada, New Mexico, and Idaho.

Uranium occurs in small quantities in most phosphate deposits. The Florida land-pebble deposits contain about 0.015 percent U_3O_8, and uranium has been recovered as a byproduct from the production of phosphoric acid. Phosphate beds of the Phosphoria formation underlie parts of Utah, Idaho, Wyoming, and Montana, and contain around 0.012 percent U_3O_8.

The broad and indefinitely bounded area in which uranium and uranium-rich rocks are relatively abundant has been defined as a uranium province. Such areas are believed to be the most favorable areas for large-scale prospecting for new uranium deposits. The chief provinces are considered to be as follows:

1. The Colorado Plateau and the surrounding areas of uranium deposits extended from the Black Hills southward through the Front Range to New Mexico and Arizona, and northward through Utah and Idaho into eastern Washington. Sandstone deposits dominate, but veins, pegmatites, uraniferous lignites, black shales, and uraniferous phosphates are present.
2. The Rim of the Canadian Shield, ranging in a narrow belt from the Bancroft area through Blind River, Manitoba, and Goldfields to Great Bear Lake. This province contains veins, pegmatites, and contact deposits mostly in Precambrian rocks.
3. Eastern Brazil in Espirito Santo, Sao Paulo, Minas Gerais, Rio Grande do Norte, and Paraiba where granitic pegmatites and pitchblende-gold in conglomerates predominate.
4. Western and Central Europe from Urgeirica (Portugal) through the French Le Massif Central, to Erzgebirge (East Germany), and Joachimsthal (Czechoslovakia) and including Cornwall, England. This province contains mostly vein deposits.
5. U.S.S.R., probably in the Ferghana-Kara region where disseminated sandstone deposits are known.
6. Southern Africa in a discontinuous belt from the Congo (Leopoldville) (Katanga) south through Rhodesia to Republic of South Africa (Witwatersrand) and southeastward to Mozambique and Malagasy. Uraniferous conglomerates, pegmatites, replacement, and vein deposits are found here.
7. Eastern Australia, including Darwin-Katherine area (Rum Jungle) Northern Territory; Mt. Isa in Queensland; Broken Hill, New South Wales; and Radium Hill, South Australia. Replacement and vein deposits predominate.

Prospecting and Exploration

The discovery of uranium ore is made difficult by the size and shape of the ore bodies, their erratic distribution, and the frequent lack of outcrops. Because of the intensive prospecting efforts from 1948 to 1960, it is likely that most of the outcropping deposits have been found, and prospecting hereafter will require subsurface methods.

Systematic exploration for uranium mineralization requires the study of geologic features,

application of radiometric or geochemical techniques, and ultimately the use of subsurface methods. Knowledge of uranium geology has advanced rapidly, and all the known characteristics of uranium occurrences are helpful to the prospector. In most areas, the occurrences are confined to certain formations, and in others the genesis of ore depended on the relationship of permeable and impervious formations. The ratio of mudstone to sandstone, for instance, proved useful in one extensive prospecting program, and the bleaching of Moenkopi beds from dark red to light yellow indicated the presence of former water channels and the possibility of mineralization. Structure of the rocks, such as faulting and folding, often plays an important part in the deposition of ore (*14*).

Radiometric methods have been of great importance in prospecting. Uranium and thorium minerals are radioactive, and this provides a major advantage over prospecting for other minerals. The *Geiger-Muller counter* was the first portable instrument. When the tube of a Geiger counter is placed near a source of radioactivity, the radiations produce pulses of electric current which can be amplified and can be used to actuate a meter, flash a neon light, or produce an audible click in a headphone. The *Scintillation counter* is more sensitive than the Geiger counter. Radioactivity occurs everywhere, as all rocks contain minute amounts of uranium and thorium, and cosmic rays are continually striking the earth from outer space, hence, a counter will always show a *background* count and only the radioactivity above that is important. Prospecting with a counter varies from tests of individual specimens and outcropping rocks to systematic radiometric surveys of extensive areas, which may include airborne surveys as well as ground surveys. From 1950 to 1960 AEC and the U.S. Geological Survey, acting for AEC, made many airborne anomaly maps which showed the location on the public domain of surface areas of high radioactivity.

Geochemical methods have been used to a slight extent in recent years and have good possibilities for the future. A study of the relative abundance of the elements is involved, and the methods depend on the analysis of trace amounts of uranium or other indicator elements in soil or rock. Considerable technical knowledge of chemistry and analytical techniques is necessary, but the method is relatively cheap and rapid. A phase of the subject is geobotanical prospecting, in which the uranium content of plant ash is analyzed. Uranium deposits as deep as 60 feet have been detected chemically in surface vegetation (*13*).

The final appraisal of an ore body requires delineation of its extent and thickness. If the ore body outcrops on the surface, some of the work can be done by surface sampling, but in most cases it must be done by exploration mining or drilling. Drilling is the most economical method of exploration. About 9 million feet of drilling was done annually during the peak of the domestic uranium exploration program in 1956–58. The Ambrosia Lake, N. Mex., ore bodies were discovered at depths of about 300 feet by drilling. Other ores in the district are as deep as 1,500 feet.

The diamond core drill was used extensively on the Colorado Plateau in early exploration drilling. The wire-line method of extracting core is satisfactory in well-consolidated rocks, but in drilling through loose overburden or unconsolidated rock formation, the core can be frozen by circulating a chilled low-temperature fluid, such as dewaxed diesel oil cooled with dry ice, to form solid cohesive cores. Cheaper methods of drilling have become popular, particularly for development drilling. Noncore drilling methods utilize rotary-table, swivel-head, cable-tool (churn), or pneumatic-percussive drills. Much exploration is done under contract with firms that specialize in drilling (*15*).

Mining

The mining of uranium ore can be classified broadly into open-pit and underground methods. In 1963, almost 3.5 million tons of ore valued at $19.67 per ton (including $0.11 for byproducts), together with 36.5 million tons of waste was mined in the United States by open-pit methods; while an almost identical amount of ore valued at $20.55 per ton (including $0.16 for byproducts), together with 1 million tons of waste was mined by underground methods.

Open-pit mining is particularly well adapted to flat beds of ore that lie relatively near the surface. A few shallow deposits covered with loosely consolidated soil or detritus could not be mined by any other method. In other cases, the choice of method depends fundamentally on the relative mining costs for the required output and often presents a complex engineering problem. Size, shape, grade, depth, and thickness of the ore body must be considered. Stripping overburden may be a large part of the cost of mining, and the depth that may be removed depends on its character and accessibility. Some may be mined to depths of more than 500 feet, but as overburden above the ore zone increases over 300 feet, underground methods may become more feasible (*6*).

Front-end loaders, small gasoline or diesel shovels, and trucks have been used to mine small deposits within 30 feet of the surface. Bulldozers are often used to shove loose overburden to one side, with wagon drills and jackhammers being used where drilling is necessary. Sinuous

and irregular masses of ore are easily followed with this equipment. In larger operations, stripping to depths of 60 feet can be accomplished economically by power shovel and dragline. Since 1959, virtually all stripping in the larger operations has been done by rubber-tired motor scrapers, pushed when loading by crawler tractors. Crawler tractors are often equipped with rippers, and drilling and blasting are seldom necessary.

Ore and waste removal from the ore zone is done with small shovels, front-end loaders, draglines, and backhoes. Backhoes are particularly effective in removing small pockets or erratic seams. Ore grade control is important in uranium mining, and each mine must develop methods that are suitable for its particular ore body. Most mines resort to stockpiling and blending, and blended material is controlled principally by chemical analyses.

Stripping is often done under contract by earth-moving firms, and costs in 1962 for motor-scraper operations ranged from 10 to 12 cents per yard at 50 feet of depth to 32 to 45 cents at 225 feet of depth. Excavation costs with trucks and 1½- to 2-cubic-yard power shovels ranged from 25 to 50 cents per cubic yard. Ore and waste removal ranged from 40 cents to $1 per ton. Ore control costs ranged from 25 to 80 cents per ton. Haulage costs from stockpiles to mills, usually done by contract, were from 4.5 to 6 cents per ton-mile. Diesel tractor trucks, hauling 20 to 90 tons, are used.

Underground uranium mines use many mining methods and variants because the ore bodies are erratic in shape, size, attitude, and grade. In the early days on the Colorado Plateau, most of the deposits were developed by adit or inclines that followed mineralized outcrops from the rims of canyons or mesas. The discovery of larger and deeper ore bodies made development and mining more complex. The trend towards mechanization has been significant. Few outcropping deposits are unexplored, and new discoveries are being made away from canyon rims or are in relatively flat country, and entry by shaft or incline is more common.

Mining of the smaller ore bodies is usually done by open stoping methods, which may be unsupported or supported by roof bolting and, in the wider places, pillar supports may be used often approaching a room-and-pillar method. Timbering is used scantily around working openings and in emergencies. Very small, irregular ore bodies may be mined by gophering where the ore is followed and mined as found. Development and mining are carried on simultaneously, and many small mines operate with practically no measured ore reserves. Long-hole drilling of walls, roof, and floor is used as an effective means of exploration. Drillings are tested with a Geiger counter or chemical analysis and sometimes the holes are probed. The operator follows the ore by checking the working face with a counter after each round. Separate blasting of ore and waste is often necessary to maintain ore grade (*4*, *5*).

Mining equipment in the small mines varies. Jackleg drills are popular, and jumbo mountings are used in development work in many mines. Transportation may vary from rubber-tired wheelbarrows in gophering operations to hand tramming, animal haulage, and mechanical haulage; any of these can be either the track or trackless type. Motive power for mechanical haulage may be compressed air, storage batteries, or diesel engines. Shuttle cars are often used, and, ore loading varies from hand-mucking to loading by scrapers or mucking machines. The track-mounted overhead mechanical loader is popular (*3*).

The larger mines differ mainly in that planned methods of ore extraction can be applied. Deposits, typically, may range from 300 to 500 feet wide and from 1,200 to 2,200 feet long, with a thickness of 5 to 20 feet. Depth of burial may be 300 feet or much more. The larger shafts are steel or concrete lined and are usually sunk using mechanical shaft muckers.

Mining methods used in the larger ore bodies include the room-and-pillar, longwall retreat, and panel methods. Modifications of each are common, and some features of each may sometimes be found in all three methods (*3*, *4*, *5*). Sublevel haulage is usually used in these operations, the haulage level being driven about 50 feet below the ore horizon and a series of vertical raises to workings in the ore body provide ore transfer and some storage (*2*). Haulageways are sometimes large enough—up to 12 by 15 feet—to accommodate large, trackless haulage equipment. In other cases electric trolley locomotives are used.

In a typical room-and-pillar operation, rooms are about 20 feet wide with the heights depending on the thickness of the ore, usually a maximum of 20 feet. Pillars 50 to 80 feet square are left and can be recovered when retreating from a mined-out area. Drill jumbos, comprising two or more hydraulic booms carrying air drills, are mounted on diesel driven tractors. One miner can drill up to 100 rounds per shift, and about 200 tons of ore is broken per round. Roof bolting, sometimes with chain-link fencing, is required.

In developing an ore body for the longwall retreat method, cuts are made at right angles both ways from a central haulageway on the ore level. Ore broken in the cut is dragged to this haulageway by slusher hoists and loaded by mucking machine into cars to be hauled to a

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transfer raise which leads to the main haulage level below. Two rows of retractable steel props on about 4-foot centers are erected in the completed cut, and they support the ground while the next cut is being made. As each cut is completed, the outer row of steel props is removed and re-erected as an inner row. The mined-out area tends to cave as the cuts retreat, but if it does not do so, previously drilled holes are loaded and blasted. This keeps the roof in the mining area from becoming dangerously stressed.

The panel method has some similarities to both the room-and-pillar and the longwall retreat methods. As in the other two methods, a working or slusher drift is driven along the bottom of the ore body, a sublevel haulage drift is driven below it and the two are interconnected at intervals by ore passes. Ore is systematically blocked out along the slusher drift and, beginning at the far end, mining is started. Rooms about 12 to 15 feet wide are driven perpendicular to the slusher drift, and pillars about 6 feet wide are left between the rooms. Ore is removed from the rooms by slusher hoists which drag lightweight scrapers carrying the ore to transfer raises. When the room is mined out, the pillar is mined, and the ore is recovered with slushers or scrapers. If the roof fails to cave soon after ore removal, it is blasted. Ore recovery with this system approaches 100 percent.

Water is not a big problem in the Colorado Plateau mines. Some mines in Arizona and Utah scarcely produce enough water to supply requirements. At Ambrosia Lake, N. Mex., the ore is in water-saturated sandstone, and the water-saturated ground above the ore was unstable. However, after the ore bodies were drained by the sublevel drifts, the ore and roof rock became more stable.

Ventilation is a problem in uranium mines because of the presence of radon and its radiation hazard. (See Radiation Hazards.) The Division of Occupational Health, U.S. Public Health Service, suggests that at least 500 cubic feet per minute of fresh air be directed to dead-end workings, or 1,000 cubic feet per minute where high concentrations of radon are found. For large stopes or areas, these figures should be increased to 1,000 and 2,000 cubic feet per minute, respectively. Fresh air should be delivered to within 30 feet of the working area. Forced ventilation may be induced by blowers or exhaust fans, directing the air to working areas by doors or ventilation tubing. Secondary ventilation openings can be supplied by large drill holes, 10 to 36 inches in diameter. These are drilled to intersect workings near mining faces, with exhaust fans at their collars. Radon gas and mine dust are thereby removed from these areas without contaminating the rest of the mine. The large 36-inch holes also can serve as escapeways (*1*).

Operating costs in underground mines, including direct and indirect mining costs, exploration, development, and amortization, have ranged from about $11 to nearly $20 per ton of ore mined in the larger developments. In the smaller mines direct and indirect mining costs and exploration drilling ranged from about $12 per ton of ore to as high as $45 in a small high-grade carnotite mine in Colorado, where no breakdown was made between mining and development costs.

Uranium Ore Processing (*2*)

The processing of uranium ores to produce required end products can be divided into the following stages: (1) mill concentrating, (2) refining, and (3) production of the purified end product. Mill concentrating is done by hydrometallurgical leaching methods using either dilute sulfuric acid or alkaline carbonate solutions. Leaching is accomplished with conventional equipment and techniques, but the recovery of uranium from leach solutions involves new techniques. The secondary minerals of the carnotite type, in which the uranium is in the hexavalent form, are rapidly soluble in dilute acid or carbonate solutions. Primary minerals, principally uraninite, coffinite, and uranothorite in which the uranium is quadrivalent, require an oxidizing agent for solution in either acid or alkaline solutions. Fine grinding may be required to insure that uraninite is accessible to the leaching solution. Oxidants added to the leach solution include soluble ferric salts and manganese dioxide or sodium chlorate in the presence of dissolved iron.

Beneficiation of ores prior to leaching has been successful in some cases. Attrition grinding has been used on low-grade ores where the standstone gangue is coarse-grained and loosely cemented with carnotite and a minimum of clay or other friable gangue minerals. Both wet and dry methods have been used. One wet mill ground the crushed ore with rod mills, and desanded the pulp in classifiers and cyclones. The sands were discarded, and the slimes containing 65 to 70 percent of the U_3O_8 and V_2O_5 were sent to leaching. Feed containing 0.04 percent U_3O_8 and 0.4 percent V_2O_5 was upgraded to 0.25 percent U_3O_8 and 2.0 percent V_2O_5, the concentrate comprising about 10 percent of the original ore weight.

A dry upgrader used an Aerofall mill, and the ore was dried concurrently with hot air that swept out the fines for collection as a concentrate in dry cyclones. The coarse material was given a quick leach with acid solution to extract additional uranium. Feed containing 0.25 percent

U_3O_8 was upgraded to about 0.9 percent U_3O_8 in 25 percent of the original ore weight.

Flotation has been tried in a number of circuits but has worked best where a sulfide concentrate, such as pyrite or chalcopyrite, or calcareous impurities could be removed from the ore. Some South African ores are floated to remove pyrite which is required for acid making.

Leaching with sulfuric acid is favored for ores that have small amounts of lime or lime-consuming minerals. Uranium is recovered from leach solutions by either ion exchange or solvent extraction, and variations of the process are based on different methods of accomplishing this. One of the big problems in leaching is to separate the pregnant solution from the solids. Preroasting the ores or adding certain flocculating agents to the leach pulp aided the thickening and filtering of some ores, but had little effect on others. A number of reagents, such as cactus extract, guar and other vegetable gums, glue, and a number of synthetic compounds, were developed and are used as aids in filtering and thickening.

Ion exchange is based on an exchange of ions between a solution and an insoluble resin. This method is particularly applicable to the removal of small amounts of solutes from large volumes of solutions. Anion exchange resins used for uranium recovery are high molecular-weight organic polymers. They contain immobile amine groups and associated mobile ions such as chloride or hydroxyl ions. The resins are virtually insoluble but are porous and contain about 50 percent water so that the mobile ions can diffuse through the resins. In practice, the resins are contacted with the leach solution and the uranium is adsorbed by the resin. While the theory of ion exchange is quite complex, for all practical purposes the uranium passes into the resin molecule in exchange for another anion. The reaction, which is reversible, may be expressed by the following generalized chemical equation, where R^+ represents the fixed portion of the ion-exchange resin, and X^- represents either NO_3^-, Cl^-, HSO_4^-, or $\frac{1}{2}$ $SO_4^=$ ions:

$$4R^+X^- + UO_2(SO_4)_3^{-4} = (R^+)_4UO_2(SO_4)_3^{-4} + 4X^-.$$

Typically, the complex uranium ion in the pregnant leach solution is exchanged for a nitrate (NO_3^-) ion. After the resin is almost saturated or loaded, it is washed free of all leach solution and then it is eluted. In this particular example, the eluting solution or elutriant could be one containing ammonium nitrate. The ion-exchange reaction under these conditions would be reversed from the loading cycle, taking the uranium ion back into solution and replacing the NO_3^- ion in the resin for reuse in the loading cycle. The concentration of uranium in the elutriant is usually much greater than it was in the original leach solution and is recovered from the elutriant by precipitation with ammonia, magnesia or other base, yielding yellow cake, the final mill product.

Ion exchange is essentially a batch operation, but continuous operation is achieved by using multiple units of equipment with staggered operating cycles. In conventional systems the resin beds are in a fixed position in packed columns and the clarified pregnant uranium solution passes through a series of columns. When the first column of the series becomes saturated (loaded), it is removed from the circuit and a newly regenerated column is added to the end of the series. The loaded column is washed and backwashed to remove any sediment and to rearrange the resin particles to prevent channeling. Then, the column is eluted, washed, and is again ready to reenter the loading circuit. Elution is usually done in multistages, which aid in removing all the uranium and producing a richer eluate.

A special adaptation of ion-exchange recovery is the resin-in-pulp (RIP) method. It has the advantage of being able to extract uranium directly from slime pulp, eliminating the clarification steps. After leaching, the pulp is desanded in classifiers and cyclones, and the sands are washed before being discarded. The pulp, now contains only slimes and dissolved uranium. If this slurry was to be passed through a fixed-bed resin unit, solid slimes would accumulate between the resin particles. To prevent this from happening, the resin is contained in rectangular baskets made of stainless steel screen. The baskets are connected to a crankshaft which raises and lowers each one 5 to 10 times per minute in a tank containing the slime pulp. Up to 15 such baskets in series may constitute a bank and the desanded pulp flows into one end continuously. The up-and-down movement of the baskets is sufficiently violent to keep the slimes in suspension and prevent silting, while at the same time giving good contact between solution and resin. Resin for the RIP process is usually made in the form of spherical beads which also help prevent silting. The beads are between 10- and 20-mesh in size. Resin life is usually 2 years or more.

Solvent extraction (SX) is another method of recovering uranium from acid pregnant leach solutions and is also used in uranium refining and fuel reprocessing. The solvent-extraction process consists of intimately contacting the uranium solution with an immiscible solvent, usually kerosine containing a dissolved organic compound. Organic compounds used include some long-chain alkyl phosphates and amines,

di-2-ethylhexyl phosphoric acid (EHPA) being among the most important with tributyl phosphate (TBP) as an additive. Such compounds are functionally similar to the anion-exchange resins and the reactions are similar. A typical amine reaction may be expressed as follows:

$$(R_3NH)_2SO_4 + UO_2(SO_4)_2^{=} = (R_3NH)_2UO_2(SO_4)_2 + SO_4^{=},$$

where R is the organic radical. As with ion-exchange resins, the reaction is reversible.

Uranium ore is leached with dilute sulfuric acid by standard procedures, and a clear pregnant solution is delivered to the solvent extraction plant. Here the solvent extractant and aqueous leach solution are mixed together violently by turbine mixers or high-speed agitators then allowed to settle into two layers, with the kerosine-solvent mixture coming off the top and aqueous solution passing out the bottom. Usually the two solutions pass countercurrently through at least four mixer settlers that sometimes are designed as a single piece of equipment. After extraction, the aqueous solution, called the raffinate, usually contains less than 0.01 gram U_3O_8 per liter and is discarded. The uranium-rich solvent may be stripped of its uranium with soda ash solution. Solvent and stripping solution are intimately mixed and settled in a series of mixer settlers in which the two liquids move countercurrently, very similar to that used in the extractant circuit. Stripped organic liquid is regenerated in this operation and is recycled to the extractant circuit, while the aqueous soda ash solution, now carrying the uranium, goes to precipitation.

Uranium is recovered from the soda ash solution either by neutralizing with acid with subsequent alkaline precipitation or by adding caustic soda to precipitate the uranium as yellow cake. The uranium precipitate is recovered by filtration, then dried and packed in drums for shipment. Causticized soda ash solution may be regenerated by carbonation, but the sulfate solution produced by acid precipitation goes to waste.

Radium, which is always present in uranium ores, is slightly soluble in the leaching process but is not recovered and remains in the waste liquors. Such waste must be handled properly to prevent contamination of streams or underground waters. The Bureau of Mines has conducted investigations of the problem in several mills. The best methods, to-date, consist of (1) recycling of the raffinate, (2) providing for soil seepage and treating the solution with a barium salt which tends to precipitate and immobilize the radium. The problem has not yet been solved satisfactorily.

Refining (*7, 8*)

Uranium metal and compounds used in the production of plutonium and for nuclear reactors require a high degree of purity. Modern feed-materials processing is conducted on a large scale using conventional chemical-engineering equipment, but the purity requirements of the product are those of the fine-chemical or pharmaceutical industries.

Three final products form the principal products: Uranium hexafluoride for isotope enrichment, uranium metal for plutonium production and other reactors, and uranium dioxide for reactor fuel elements. The normal processing stages are the preparation of orange oxide (UO_3); conversion of orange oxide to brown oxide (UO_2); and the fluorination of UO_2 to produce green salt (UF_4), part of which is reduced to uranium metal and the rest is fluorinated to UF_6.

Yellow cake from the mills is dissolved in nitric acid, and the resulting uranyl nitrate, $UO_2(NO_3)_2$, solution is extracted by solvent extraction with a countercurrent flow of a solution of TBP in hexane or kerosine. TBP is highly selective in extracting uranyl nitrate from the digest liquor. This is heightened by giving the loaded organic a light scrubbing with water. The aqueous scrub-solution is recycled and the purified uranyl nitrate is recovered from the organic solvent stream by mixing with pure water. After settling, the stripped solvent stream is recycled to the primary extraction mixer, and the pure aqueous solution is boiled down to molten uranyl nitrate hexahydrate which is then denitrated to produce UO_3. Until recently, the denitration was done batchwise by heating the solid uranyl nitrate in gas or electrically heated, stainless steel pots at atmospheric pressure, but is now being done in a continuous fluid-bed denitrator.

UO_3 is reduced to UO_2 in a two-stage fluidized-bed reactor at 650° to 800° C, using hydrogen as a reductant. Interest in UO_2 as a reactor fuel is growing, and this may be the end product for power reactors. For isotopic enrichment in the gaseous diffusion plants and for the production of uranium metal, uranium tetrafluoride (UF_4) is required as an intermediate. UF_4 is produced by reacting UO_2 with anhydrous hydrofluoric acid (HF). Anhydrous HF at 120° C is introduced countercurrently to UO_2 which is being moved by motor-driven spiral screws along a long cylindrical reactor. The reaction is highly exothermic and rises to about 600° C near the end, where the HF enters and the UF_4 discharges.

Uranium metal is prepared by metallothermic reduction of UF_4 with magnesium in a bomb

reactor. UF_4 and magnesium chips are blended and charged into a steel reactor lined with magnesium fluoride. After charging and capping, the bomb is placed in an electric or gas-fired furnace and heated to about 600° C. Complete reaction requires up to 10 hours, and a regulus of uranium metal about 17 inches tall and 17.5 inches in diameter, weighing almost 3,000 pounds, is produced. Other methods of producing uranium metal include reduction of UF_4 with calcium and sodium, reduction of oxide with calcium and aluminum, electrolysis of fused salts, and decomposition of uranium hydride (UH_3), above about 310° C in a vacuum.

UF_6 is made by reacting UF_4 with elemental fluorine. A monel reactor heated to about 500° C is used and the UF_6, which sublimes at 56.4° C, volatilizes and is deposited as a solid on a cold surface. The UF_6 is shipped to gaseous diffusion plants, where it is enriched in the U^{235} isotope. The separating media in a gaseous diffusion plant are porous barriers, through which the lighter $U^{235}F_6$ vapor diffuses slightly more rapidly than does the $U^{238}F_6$, and a partial enrichment in U^{235} is achieved. In each passage, the proportion of U^{235} is raised a factor of about 1.0014; therefore, to obtain 99 percent pure U^{235} requires about 4,000 diffusion stages. The diffusion plant at Oak Ridge, Tenn., was designed with hundreds of acres of diffusion barriers and thousands of miles of piping.

The fabrication of fuel elements for reactors is extremely complex and involves so many metallurgical and fabrication techniques that it can only be mentioned here. The reader can find many comprehensive texts on the subject (*12*).

Plutonium 239 (Pu^{239}) is produced by irradiation of U^{238} metal in a production reactor. Neutrons captured by the U^{238} produce highly radioactive U^{239}, which decays with a half-life of 23.5 minutes to neptunium 239 (Np^{239}). This in turn decays with a half-life of 2.3 days to Pu^{239}. Pu^{239} is an alpha-emitter with a fairly long half-life of 2.44×10^4 years. The metal is highly reactive and is very difficult to handle because it is one of the most toxic radioactive materials known. It may enter the body through inhalation, ingestion, and absorption through the skin. Once ingested it enters the blood stream and is rapidly assimilated in bones, where most of it will remain indefinitely.

Pu^{239} is also produced in any power or production reactor using fuel elements that contain the U^{238} isotope. Some power reactors, particularly those operating on natural uranium fuel or that have natural or depleted uranium blankets, produce Pu^{239} as a byproduct, which is potentially usable as fissionable fuel. Production reactors are designed especially to produce Pu^{239}.

Natural-uranium metal used in production reactors is encased in aluminum cans prior to being charged into the reactors. After several months' irradiation, the cans are pushed out of the reactor into a canal filled with 30 feet of water. After a month or so of "cooling" to permit some of the intense short-lived radioactivity to die, the cooled elements are sent to the fuel reprocessing plant where the fission products, the Pu^{239}, and residual uranium are separated. Beyond this point, the processing of Pu^{239} for military use is under strict security. Some Pu^{239} is being tested in the Plutonium Recycle Test Reactor (PRTR) at Hanford to demonstrate the feasibility of using plutonium as fuel for civilian power reactors.

USES

Uranium has been used principally for atomic weapons, but the development of nuclear reactors is proceeding methodically and this will be the principal use in the future.

A nuclear explosion occurs when two or more subcritical masses of fissionable material are brought together and held together long enough for a supercritical state to develop. The first bomb dropped over Hiroshima, Japan, was made with U^{235} and the second one, dropped on Nagasaki, was composed of plutonium; each had a detonation yield of approximately 20,000 tons of high explosive, yet weighed only about 10,000 pounds completely encased. The most sophisticated and destructive weapon known to man is the thermonuclear device, known as the hydrogen bomb or H-bomb, the energy of which is created by fusion. Heat and pressure from a fission explosion is used to initiate the fusion reaction.

Nuclear explosives are also being developed for peaceful purposes under the AEC Plowshare program discussed under Research.

Nuclear reactors can be divided broadly into four categories based on their uses—(1) electric-power reactors, (2) propulsion reactors, (3) research and development, testing, and medical therapy reactors, and (4) space and process heat reactors, particularly water desalting.

The great promise of nuclear energy lies in the application of nuclear reactors to electric-power production and propulsion. With a wide variety of fuel, fertile material, coolants, geometry, and types of moderators available, some 900 combinations of reactor design are possible and as many as 100 of these may be feasible. The principal civilian nuclear power reactors in operation, under construction, and under consideration as of December 31, 1963, are shown in table 3. Only reactors with an electrical capacity of over 10,000 kilowatts are listed. In

addition to the 22 listed, 9 smaller electric-power experimental reactors were operable, 5 were being built, 2 were planned, and 8 were operated in the past and dismantled, making a total of 47 power reactors that have developed data on nuclear power.

In addition, 69 military reactors, including those on 3 surface ships and 34 submarines were in operation; and 58 more were being built and 3 planned. Also a total of 125 test, research, and teaching reactors were operable, being built, or planned.

In the United States, the boiling-water and pressurized water reactors are currently the best contenders for full-scale power generation, and a number of companies have selected these for major development. General Electric Co. and Allis-Chalmers Manufacturing Co. are promoting boiling-water reactors, and Westinghouse Electric Corp. and Babcock & Wilcox Co. favor pressurized-water reactors. Atomic Energy of Canada, Ltd., has been developing a pressurized-water reactor that uses natural uranium with heavy water for moderator and coolant. India is constructing a heavy-water reactor and a boiling-water reactor. The British have favored a high-temperature, gas-cooled graphite-moderated reactor using natural uranium. The Peach Bottom, Pa., reactor is a similar type and was built by General Atomic Division, General Dynamics Corp. as a prototype facility.

TABLE 3.—*Principal civilian nuclear power reactors* [1]

Reactor	Location	Electrical capacity, kilowatts	Initial criticality
Operable:			
Shippingport Atomic Power Station	Shippingport, Pa	[2] 60, 000	1957
Dresden Nuclear Power Station	Morris, Ill	200, 000	1959
Yankee Nuclear Power Station	Rowe, Mass	175, 000	1960
Big Rock Nuclear Power Plant	Big Rock Point, Mich	73, 800	1962
Elk River Reactor	Elk River, Minn	[3] 23, 000	1962
Indian Point Unit No. 1	Indian Point, N.Y	[3] 255, 000	1962
Hallam Nuclear Power Facility	Hallam, Nebr	75, 000	1962
Humboldt Bay Power Plant	Humboldt Bay, Calif	48, 500	1963
Piqua Nuclear Power Facility	Piqua, Ohio	11, 400	1963
Carolinas-Virginia Tube Reactor	Parr, S.C	[3] 17, 000	1963
Enrico Fermi Atomic Power Plant	Lagoona Beach, Mich	60, 900	1963
Experimental Breeder Reactor No. 2	Idaho Falls, Idaho	16, 500	1963
Total operable capacity		1, 016, 100	
Under construction:			
Boiling Nuclear Superheat Reactor	Puente Higuera, P.R	16, 300	1964
Pathfinder Atomic Power Plant	Sioux Falls, S. Dak	58, 500	1964
Peach Bottom Atomic Power Station	Peach Bottom, Pa	40, 000	1965
La Crosse Boiling Water Reactor	Genoa, Wis	50, 000	1965
Experimental Gas-Cooled Reactor	Oak Ridge, Tenn	21, 900	1965
San Onofre Nuclear Generating Station	San Clemente, Calif	375, 000	1966
Connecticut Yankee Atomic Power Station	Haddam Neck, Conn	463, 000	1967
Jersey Central Power & Light Co	Oyster Creek, N.J	515, 000	1968
Under consideration:			
Malibu Nuclear Plant	Corral Canyon, Calif	463, 000	1968
Niagara Mowhawk Power Co. (Nine Mile Point)	Oswego, N.Y	500, 000	1968

[1] Including experimental reactors of over 10,000-kilowatt generating capacity.
[2] An increase to 150,000 kilowatts was scheduled for mid-1964.
[3] Including organic-fueled superheat.

NOTE: Power conversion equipment will utilize heat from the New Production Reactor at Hanford, Wash., for generating 800,000 kilowatts in 1966.

Source: Updated from AEC Annual Report for 1963, pp. 75–90.

The development of nuclear energy for water desalting is gaining in importance in the United States and in other countries where potable water is a problem. The International Atomic Energy Agency has undertaken to exchange technical information between interested countries, particularly Israel, Tunisia, Mexico, the Soviet Union, and the United States. In this country, the Department of the Interior and AEC, in consultation with the Office of Science and Technology are collaborating on an aggressive and imaginative program for a large-scale plant to desalt sea water.

Radioisotopes are useful products obtained from special reactors and from the reprocessing of partly burned nuclear fuels. More than 1,000 different radioisotopes have been identified, but most are either too difficult to produce or have too short a half-life to be of practical value. About 100 different ones are useful and com-

prise over 12,000 shipments per year made by AEC at the Oak Ridge National Laboratory, Oak Ridge, Tenn. They are used as a substitute for X-rays for inspecting castings and welds; for sterilizing drugs, medical supplies and foodstuffs; as a power source for small quantities of electricity; gaging control of industrial operations; and many tracer or activating uses.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Much of the vanadium produced on the Colorado Plateau is a byproduct of the roscoelite-carnotite ores. These were mined for their vanadium content long before uranium came into prominence.

Thorium is found in the thorianite-uraninite deposits of the Bancroft Region and in the uranium ores of the Blind River area both in Ontario, Canada. Thorium is recovered as a byproduct from the processing of uranium at the Elliot Lake plant of Rio Tinto Dow, Ltd.

Some of the gold ores of the Republic of South Africa carry recoverable quantities of U_3O_8, in recent years yielding around 0.4 to 0.5 pound U_3O_8 per ton and 0.3 ounce of gold per ton. Other ores in the Transvaal have been primarily uranium producers with about 1.3 pounds U_3O_8 and only about 0.1 ounce of gold recovered per ton of ore.

Uranium also occurs in the land-pebble phosphate deposits of Florida, but the quantity is only about 0.015 percent. A process, nevertheless, was worked out and operated for several years at one of the phosphate plants. The cost of recovery was too high to compete economically with uranium from the Colorado Plateau and large areas of phosphate rock are being mined out without recovering the uranium.

Molybdenum and vanadium occur in the uraniferous lignites of North and South Dakota. These lignites are burned and the ash sent to various mills where molybdenum is leached along with the uranium and, to some extent is recovered separately. The slime tailings from the uranium circuit carry vanadium and a separate recovery system has been installed to recover it.

Copper occurs in recoverable amounts in uranium ore deposits near the Arizon-Utah boundry. A sulfide concentrate is recovered by flotation but requires acid-leaching to remove a small amount of uranium before being sent to a copper smelter. Not all of the copper is recovered by flotation, and most of that remaining is leached with the uranium, where it is recovered by cementation on scrap iron.

Major byproducts of uranium fission are the "atomic ashes" or fission products formed in splitting uranium nuclei into lighter elements. The fission products are a mixture of more than 30 elements, from zinc (atomic number 30) to gadolinium (atomic number 64). About 200 different isotopes have been identified, but only about 80 are produced in fission. The major fission products and the approximate weight percentage present in spent reactor fuel after a 100-day cooling-off period are—

	Percent		*Percent*
Strontium 90	3.8	Ruthenium 103	5.0
Barium 131	4.0	Neodymium 147	10.0
Yttrium 91	2.3	Xenon 133	10.0
Lanthanum 140	4.0	Cesium 137	10.0
Cerium 141	10.1	Molybdenum 99	8.0
Zirconium 95	9.9	Praseodymium 144	4.5
Columbium 95	4.7	Samarium 153	3.0
Tellurium 125	1.2	Technetium 99	2.7
Iodine 129	.6		

Nearly all fission fragments are radioactive, emitting negative beta particles. Many of the products emit gamma rays in addition to beta particles, representing the so-called delayed fission gamma radiation which presents many shielding problems.

The nuclear age has placed emphasis on the development of new special and high-purity materials. These include beryllium, zirconium, hafnium, boron, and cadmium, which are discussed in separate chapters. Other materials, which have a large capacity for capturing neutrons, require development.

ALTERNATE MATERIALS

No immediate substitutes exist for uranium as a nuclear fuel; thorium may complement uranium in nuclear reactors within the next decade. A great international interest in thorium exists, and it is felt that the long-range possibilities of nuclear power include the use of uranium 233 derived from thorium 232.

Controlled release of energy from fusion in thermonuclear devices offers the potentiality of an essentially unlimited source of energy. However, practicality of electrical power from fusion will be dependent upon successful solution of a great multitude of formidable problems.

SECONDARY RECOVERY

Under current technology, about three-fifths of the uranium that enters a fuel element fabrication plant will leave in usable fuel elements. Of the remaining two-fifths, one-half can be recovered in the fabrication plant by remelting and the other half will be so contaminated with foreign matter that it must be recycled through various processing steps and returned to the original stream at appropriate points.

The quantity of atomic fuel used per cycle or fuel burnup ranges from a fraction of 1 percent to about 10 percent of the total amount of fissionable and fertile material. To utilize the equivalent of a single fuel charge in a nuclear reactor, many cycles of burnup and reprocessing recovery, or separation, operations are necessary. The separation process must remove the highly radioactive fission products as well as any accompanying structural or cladding materials from both the fissionable or fertile material; in addition, there must be a degree of separation between the fertile and fissionable material.

RESERVES

Domestic inplace uranium reserves at the end of 1963, shown in table 4, were estimated by AEC to total 66 million tons averaging 0.24 percent, or 160,000 tons of U_3O_8; these inplace reserves are distributed principally in New Mexico, Wyoming, Colorado, and Utah, with small quantities in 11 other States. These data are conservative and probably as well founded as those on any mineral commodity; they are based on uniform statistical analyses of certified and checked sample data. Basic sampling data were reviewed by AEC for accuracy, problems of the mining methods in use were considered, and estimates include only those reserves for which specific data are available. The figures, therefore, represent ore minable under present conditions at $8 per pound.

TABLE 4.—*Domestic uranium ore reserves by States as of Dec. 31, 1963*

State	Million tons of ore	Percent U_3O_8	Thousand tons U_3O_8
New Mexico	32.0	0.24	76.8
Wyoming	24.7	.24	57.0
Colorado	3.1	.27	9.3
Utah	2.3	.30	6.7
Other States (Alaska, Arizona, California, Idaho, Montana, Nevada, North Dakota, Oregon, South Dakota, Texas, and Washington)	3.9	.22	10.2
Total	66.0	.24	160.0

Free-world reserves, shown in table 5, were estimated at 612,000 tons of U_3O_8, over 87 percent being in Canada, United States, and the Republic of South Africa. Data for table 5 were derived from estimates made by AEC, U.S. Geological Survey, Canadian Department of Mines and Technical Surveys, European Atomic Energy Community (Euratom), and industrial staffs. These in turn credit various atomic-energy agencies for their original data. They have been updated to agree with papers presented at the Third Geneva Conference in September 1964. The data are based roughly on the same degree of probability in each case, and on the same criteria as the domestic reserve estimate, following the practice of AEC. Different estimates showed slight variations in a few cases, few of which would be significant.

Data on reserves in Communist-controlled countries are difficult to obtain. Probably among the best are those cited in the Robert McKinney report to the Joint Committee on Atomic Energy, October 1960, volume 4, pages 1613–18. These data list a total of 100,000 to 370,000 metric tons of uranium metal, of which 80,000 to 270,000 metric tons was estimated for U.S.S.R., 20,000 to 100,000 metric tons for China, 100,000 metric tons for East Germany, and the balance for Czechoslovakia, Bulgaria, Rumania, Poland, and Hungary. Materials of a wide range in uranium content were included, and no clear-cut distinction was made between reserves and resources in the sense used for the free-world data.

TABLE 5.—*Free-world uranium reserves by countries as of July 1964*

Country	Tons U_3O_8	Approximate grade, percent U_3O_8
Canada	210,000	0.124
United States	160,000	.24
South Africa, Republic of	150,000	.02
France [1]	40,000	.14
India	12,000	.05–0.30
Australia	10,000	.26
Portugal	7,000	.2
Spain	6,000	.12–0.70
Others, including Argentina, Brazil, West Germany, Italy, Japan, Mexico and Sweden	17,000	.02–0.15
Total	612,000	

[1] Including Malagasy Republic and Gabon.

The estimated resource of domestic uranium is very large. In the frenzied quest for sources of uranium, which began in 1944 shortly after the first self-sustaining nuclear chain reaction had taken place at Stagg Field (December 2, 1942), all known potential resources of uranium were examined and evaluated, and several were tested for possible mining methods and metallurgical recovery. Only the discovery of the high-grade western deposits relegated many of the categories to the status of resources. The magnitude and potential reasonably assured and total resources are listed in table 6. In the distant future, with increasing demand and exhaustion of deposits of the type presently exploited, the price of uranium will rise gradually into the higher categories. The successful development of breeder reactors would utilize uranium so efficiently that higher prices for U_3O_8 would have a relatively small effect on the cost of power.

TABLE 6.—*Magnitude and sources of uranium in the United States*

Group [1]	Price range per pound of U_3O_8	Reasonably assured resources of U_3O_8 (thousand short tons)	Estimated total resources of U_3O_8 (thousand short tons)
1	Under $10	[2] 380	800
2	$10 to $30	400	700
3	30 to 100	11,000	23,000
4	100 to 500	500,000	2,000,000

[1] Group 1. Measured, indicated, and inferred ores, plus geologic estimate of potential discoveries.
Group 2. Low-grade Western States uranium ores and Florida phosphate deposits.
Group 3. Tennessee shales, New Hampshire granites, and Florida phosphate.
Group 4. Granites elsewhere (to a maximum depth of 2,000 feet) and shales with extensive mining over large areas in various States.
[2] Including uranium already mined.

Source: AEC, Civilian Nuclear Power, A Report to the President, 1962, as presented to the Joint Committee on Atomic Energy, 88th Congress, Feb. 20 and 21, 1963.

Fuel Value of Uranium Resources

The total energy content of the domestic uranium resources listed in table 6 is shown in table 7. The energy values listed are the theoretical heat units that would be derived by complete fission of all the uranium including the conversion of U^{238} to Pu^{239} and its fission.

TABLE 7.—*Energy content of domestic uranium resources*

[See table 6 for quantities of fuel]

Group [1]	Uranium resources price range per pound U_3O_8	Fission energy content, Q [2]	
		Reasonably assured resources	Total resources
1	$5-$10	22	50
2	10- 30	24	40
3	30-100	660	1,400
4	100-500	30,000	120,000

[1] Group 1. Measured, indicated, and inferred ores, plus geologic estimate of potential discoveries.
Group 2. Low-grade Western States uranium ores and Florida phosphate deposits.
Group 3. Tennessee shales, New Hampshire granites, and Florida phosphate.
Group 4. Granites elsewhere (to a maximum depth of 2,000 feet) and shales with extensive mining over large areas in various States.
[2] Q=1 quintillion British thermal units, or 10^{18} Btu. 1 short ton U_3O_8 will produce 5.9×10^{13} Btu on complete fissioning.

Source: AEC, Civilian Nuclear Power, A Report to the President, 1962, Appendix II, p. 34.

In 1963, Department of the Interior Energy Policy Staff prepared a report—Supplies, Costs, and Uses of the Fossil Fuels. In this report, the known recoverable and marginal and undiscovered marginal resources of coal were estimated at 4,220 billion tons with an energy value of 88.6 Q (Q=10^{18} Btu) and the energy value of petroleum, natural gas, natural gas liquids, oil in bituminous rock, and shale oil were estimated at an additional 41.5 Q or a total energy value for all fossil fuel at 130.1 Q.

As with the fossil-fuel resources, all energy in the uranium resources will not be recoverable. Current water reactors average only about 1.3 percent utilization of natural uranium. The U^{235}, which constitutes only 0.7 percent of natural uranium, is readily fissionable, and only a small part of the U^{238} is converted to fissionable material in the simple types of reactors. Hence, improvements in fuel utilization must be achieved if nuclear energy is to become capable of supplying low-cost energy in the amounts that projected future demand indicates. Breeder reactors can convert the U^{238} portion of natural uranium into energy-producing fissionable material and might obtain 50 to 100 times as much energy from a given quantity of natural uranium as present-day reactors. However, breeder reactors are still in an early stage of development, and their successful practical application is half hoped for, half expected, in the decade 1970–80. In an efficient breeder operation, about 80 percent of the uranium will be utilized because of unrecoverable losses in processing reactor fuel and the production of unfissionable higher isotopes during breeding.

CONSERVATION

The mining of uranium ore deposits has, in general, been done very efficiently. The development of room-and-pillar and panel mining systems together with the use of roof bolts and wire mesh have resulted in almost complete recoveries of ore. A few mines have successfully developed and used beneficiation methods for upgrading economically submarginal ores, and some attempts have been made to heap-leach subgrade ore piles or to leach in place, sometimes called solution mining.

Once made into concentrate, uranium passes into custody of AEC and is accounted for very strictly. Because uranium products are very expensive, losses are kept to a minimum. For the same reason, all uranium from scrap or spent fuel is reclaimed. Even if present-day economics does not favor reprocessing, spent fuel is stored, usually in underground places, where it can be reclaimed if future generations find it feasible to rework the material.

Uranium is wasted in a few low-grade materials being mined for other uses, the most significant being the Florida phosphate rock which is mined on a large scale, but recovery of the uranium is uneconomic. The uranium dissolves and becomes a part of the phosphoric acid and eventually ends up in the fertilizer product.

SOURCES OF STATISTICAL INFORMATION

AEC provides the Bureau of Mines with quarterly reports, showing delivery of crude ore and uranium oxide content to processing plants and monthly operation reports of the processing plants. From these data and the annual Bureau of Mines canvass for mine and quarry information from mine operators annual compilations are made showing the quantity of ore and content of uranium oxide shipped to processing plants. The value of mine shipments for each shipper is based on AEC Circular 5 and Circular 5 revised. The provisions of these circulars are no longer in effect, however, payments for purchases of crude ore by mill operators are very similar to those that prevailed when they were in effect. The quantity and value of the uranium oxide recoverable from crude ore shipped to processing plants also is calculated and the data are published in the Minerals Yearbooks.

The annual mine-and-quarry information canvass also gives information on total material handled, mining methods, and exploration and development conducted, which appears under Technologic Trends in the Mineral Industries of the Minerals Yearbook, Volume I, Metals and Minerals (Except Fuels).

AEC publishes information in its annual report on the amounts of U_3O_8 received each year from domestic and foreign suppliers and also issues press releases showing the U_3O_8 content and cost of concentrate purchased. Both AEC and the Bureau respect the confidentiality of company operations, and individual company data are not published unless permission of the company has been given in writing. AEC also maintains records of ore reserves and mill stockpiles at the end of each year and publishes this information in their annual report. These AEC data are published in daily newspapers in areas where interest lies, in the technical journals, and are included in the Bureau of Mines Minerals Yearbook.

PRODUCTION, CONSUMPTION, AND TRADE

AEC has announced that it would not build up a significant stockpile of unprocessed uranium concentrate, therefore, production and consumption of uranium may be considered synonymous. Hundreds of tons of uranium are tied up by inprocess inventories, and even the uranium that enters reactors is not consumed, although it is placed in useful service. For instance, 50 tons of natural-uranium loaded into a production reactor and operated for 1 year at 28,000 kilowatts will consume about 23 pounds of U^{235} and produce almost an equivalent amount of Pu^{239}. Only about 0.1 percent of the uranium can be converted before the charge must be removed and reprocessed. Power reactors consume uranium in a similar manner, but a higher burnup (5 to 6 percent) is possible.

Table 8 shows the production and average grade of uranium ore by States from 1959 to 1963, and table 9 lists the domestic ore production and grade, the concentrate purchased by AEC of domestic and foreign origin and the total cost and per pound cost of domestic concentrate from 1943 through 1963. The data in table 9 from AEC are for fiscal years and will not match data of the Bureau of Mines in the other tables which cover calendar years. Purchase of foreign uranium by AEC is based on contracts some of which date back as far as 1947.

Uranium deliveries in short tons of U_3O_8 anticipated by AEC on existing contracts are as follows:

Fiscal year	Domestic	Canada	Overseas	Total
1964	12, 200	2, 200	3, 850	18, 250
1965	11, 600	1, 250	2, 800	15, 650
1966	10, 500	700	1, 600	12, 800
1967	8, 900	300	650	9, 850
1968	7, 800	----------	----------	7, 800
1969	7, 800	----------	----------	7, 800
1970	7, 800	----------	----------	7, 800
1971	3, 900	----------	----------	3, 900

The free-world production of U_3O_8 by countries, listed in the order of their importance, from 1956 to 1963 is shown in table 10.

Ores and concentrates are duty-free. Metals and alloys have an effective tariff rate of 25 percent ad valorem.

STRATEGIC CONSIDERATIONS

Uranium is the basis for the atomic energy program, because uranium is the only material occurring in nature that is fissionable. Defense of the Nation as well as ultimate success in armed conflict are largely based on the availability of raw materials for, and the ability to produce, atomic weapons. It also seems certain that nuclear power and other benefits of the atomic age will soon become an essential element of economic strength in the United States and in other nations.

Stockpiles of uranium in various forms are distributed throughout the uranium-production process. An inventory of concentrate will al-

TABLE 8.—*Uranium mine production by States*

State	1959		1960		1961		1962		1963	
	Short tons	U_3O_8 content, percent	Short tons	U_3O_8 content, percent	Short tons	U_3O_8 content, percent	Short tons	U_3O_8 content, percent	Short tons	U_3O_8 content, percent
Alaska	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)
Arizona	253, 390	0. 30	283, 684	0. 27	228, 225	0. 26	143, 196	0. 26	150, 584	0. 37
California	(1)	(1)	(1)	(1)					(1)	(1)
Colorado	1, 044, 089	. 26	1, 149, 583	. 25	1, 282, 462	. 22	1, 135, 440	. 21	1, 014, 206	. 20
Idaho	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)		
Montana	(1)	(1)	1, 726	. 21	729	. 19	(1)	(1)	(1)	(1)
Nevada	(1)	(1)	(1)	(1)	(1)	(1)			(1)	(1)
New Jersey			(1)	(1)						
New Mexico	3, 269, 826	. 21	3, 793, 494	. 21	3, 631, 036	. 22	3, 478, 238	. 23	2, 304, 577	. 22
North Dakota							(1)	(1)	5, 567	. 30
Oregon	(1)	(1)	(1)	(1)	2, 160	. 35	(1)	(1)	1, 763	. 30
South Dakota	45, 734	. 19	41, 104	. 19	43, 588	. 17	29, 452	. 18	72, 088	. 31
Texas	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)
Utah	1, 210, 654	. 36	1, 089, 757	. 30	1, 098, 783	. 28	781, 955	. 35	743, 792	. 37
Washington	(1)	(1)	171, 255	. 23	175, 327	. 25	(1)	(1)	117, 286	. 26
Wyoming	864, 582	. 25	1, 357, 225	. 25	1, 521, 064	. 23	1, 301, 784	. 25	1, 475, 070	. 23
Undistributed	246, 652	. 19	82, 383	. 24	57, 955	. 25	182, 805	. 26	62, 638	. 27
Total	6, 934, 927	. 25	7, 970, 211	. 24	8, 041, 329	. 23	7, 052, 870	. 24	5, 947, 571	. 25

[1] Included with "Undistributed" to avoid disclosing individual company confidential data.

TABLE 9.—*United States uranium ore and concentrate data, fiscal years 1943–1963*

Fiscal year	Ore reserves,[1] million short tons	Ore production		Concentrate procurement, short tons U_3O_8		Purchases of domestic concentrate	
		Quantity, thousands short tons	Grade, percent U_3O_8	Domestic origin	Foreign origin	Total cost (million)	Average cost per pound U_3O_8
1943–1947				1, 440	10, 150		
1948	1. 0	54. 0	0. 31	110	1, 960	$1. 7	$7. 14
1949	1. 0	89. 0	. 27	120	1, 960	2. 0	8. 53
1950	2. 0	230. 0	. 31	320	2, 740	5. 8	8. 92
1951	2. 0	290. 0	. 32	630	3, 050	12. 8	10. 01
1952	3. 0	390. 0	. 32	830	2, 830	18. 4	11. 19
1953	5. 0	610. 0	. 31	990	1, 910	24. 2	12. 30
1954	10. 0	914. 0	. 32	1, 450	3, 240	35. 6	12. 25
1955	27. 0	1, 306. 0	. 30	2, 140	3, 800	53. 6	12. 51
1956	63. 0	2, 185. 0	. 28	4, 200	6, 240	97. 8	11. 63
1957	78. 0	3, 303. 0	. 28	7, 580	8, 580	159. 6	10. 53
1958	82. 5	4, 416. 0	. 27	10, 244	16, 132	196. 0	9. 57
1959	88. 9	6, 117. 0	. 26	15, 162	18, 164	280. 5	9. 25
1960	82. 0	[1] 7, 970. 2	. 24	16, 567	18, 015	297. 0	8. 99
1961	74. 0	[1] 8, 041. 3	. 23	17, 758	14, 502	303. 0	8. 54
1962	68. 0	[1] 7, 052. 9	. 24	17, 255	12, 107	283. 0	8. 20
1963	66. 0	[1] 5, 947. 5	. 25	15, 759	11, 222	248. 0	7. 85

[1] Yearend or calendar year.

Source: AEC annual reports and press releases.

TABLE 10.—*Free-world production of uranium oxide (U_3O_8) by countries*

[Short tons]

Country	1956	1957	1958	1959	1960	1961	1962	1963
United States	6, 000	8, 640	12, 570	16, 420	17, 760	17, 399	17, 010	14, 218
Canada	2, 280	6, 635	13, 403	15, 892	12, 748	9, 641	8, 430	8, 141
South Africa, Republic of	4, 365	5, 700	6, 245	6, 445	6, 409	5, 468	5, 024	4, 532
Congo (Leopoldville)	1, 300	1, 300	2, 300	2, 300	1, 200			
France		[1] 535	[1] 755	[1] 1, 065	[1] 1, 379	[2] 2, 078	[2] 2, 601	[2] 2, 021
Australia	300	400	700	1, 100	1, 300	1, 600	1, 400	1, 200
Other countries	225	260	277	128	334	304	135	88
Total	14, 470	23, 470	36, 250	43, 350	41, 130	36, 490	34, 600	30, 200

[1] Includes Malagasy Republic.
[2] Includes Malagasy Republic and Gabon.

ways be stockpiled at the refineries, and various quantities of orange oxide, green salt, and metal will be in process inventories, or in transit between the various feed material plants. At the reactor sites, several thousand tons of uranium are undergoing irradiation. It is necessary before chemical separation to allow substantial time for decay of highly radioactive products in the irradiated metal; thus, additional hundreds of tons of uranium are in storage awaiting chemical separations. At the gaseous diffusion plants, many hundreds of tons of uranium are in various processing stages.

Practically all the uranium procured by AEC is still on hand in some form or another, assuming that plutonium is the equivalent of the U^{235} used in its production. Uranium goes so far that probably only a few percent of that procured has actually been fissioned or consumed. It has been separated or changed in form, perhaps, and stocks of source material can be classed as follows: (1) inprocess inventories, (2) plutonium produced by irradiating U^{238} in production reactors, (3) highly enriched U^{235} separated from natural uranium and delivered to the weapons stockpile, (4) enriched uranium withdrawn from the weapons circuit for research, reactor fuel, and distribution to foreign Governments, and (5) large quantities of depleted uranium for which little use is found today but which may be useful in breeder reactors in the future.

Eventually nuclear energy will be needed to meet the nation's expanding energy requirements. Present resources of coal, oil, and oil shale—with research unquestionably in time lowering their recovery costs—should last beyond the next 100 years. Nevertheless, nuclear-power development should proceed because it may require 30 or 40 years to develop breeder reactors to the point where they can become the principal source of economic nuclear power. After the introduction of breeder reactors, it will take many years to provide sufficient fissionable material to permit a fast rate of growth. It takes about 10 years for a breeder reactor to produce sufficient plutonium (or U-233, if thorium will be the fertile material used) to double reactor capacity.

Prior to the development of the nuclear bomb, uranium was an unimportant metal used in very small quantities as a ceramic coloring agent. With the development of nuclear weapons it became a prime strategic metal, and the self-sufficiency of the United States was very low. An intensive prospecting and development program was initiated, and a very successful series of bonuses, premiums, and long-term contracts built up the uranium mining industry from almost nothing in 1950 to the largest in the free world. The country is now self-sufficient in uranium and need not depend on foreign sources.

Present AEC contracts with mill operators, which carry to 1966 in most cases and to 1970 in others, will probably result in a moderate surplus of material by 1966. Means of production is vital to the future interests of the country, and the problem is to determine how best to sustain the uranium industry during the slack period.

GOVERNMENT PROGRAMS

Uranium production, like most other phases of the atomic energy program, has been developed primarily to meet a military requirement, which is still the predominant factor in determining the AEC procurement program.

Production of nuclear weapons continues at the rate authorized by the President with research directed toward improvement of current weapon models and development of new ones to meet the requirements of the Armed Forces.

The AEC was given the responsibility for regulating the possession and use of source, by-product, and special nuclear materials, under the Atomic Energy Act of 1954. Licensing arrangements permit industrial participation in programs involving source or fissionable materials. All information on military application programs is controlled by the AEC, which also regulates the construction and operation of certain nuclear facilities and the operators of these facilities.

Principal objectives of the uranium program are as follows:

1. Maintenance of uranium production for military and atomic-power requirements
2. Protection against a possible major overproduction with rapid exhaustion of large ore reserves.

When uranium was in short supply, it was necessary for AEC to make long-range commitments wherever possible and to develop new sources of production to assure requirements for the military demand. By 1958, domestic uranium production and reserves attained self-sufficiency, and it was no longer necessary to expand production. In November 1962, AEC announced a new program for domestic procurement to extend procurement time from December 31, 1966, when the present program ends. This program invited milling companies to defer a portion of the concentrates contracted for delivery before 1967 for delivery in 1967 and 1968. An additional quantity of concentrates, equal to the quantity deferred, would be purchased in 1969 and 1970.

In June 1958, AEC removed certain prohibitions on nonnuclear uses of uranium and made depleted uranium available for sale on an un-

classified basis. In August 1964, the Atomic Energy Act of 1954 was amended to permit private ownership of nuclear materials. The amended Act provided that by January 1, 1969, private power producers may buy raw uranium from mines and enrich it themselves. By January 1, 1971, all new distributions of nuclear materials must be by sale, rather than by lease as at present. By June 30, 1973, any materials leased from AEC by private firms must be purchased by those firms or returned to AEC; however, AEC will still retain its licensing and regulatory functions.

The Atomic Energy Act also directed AEC to conduct research, educational, and training programs and to otherwise develop the peaceful uses of nuclear energy. This is discussed in more detail in the section under Research.

Uranium was included in the list of minerals that were eligible for financial assistance under the Defense Minerals Exploration Administration (DMEA) program. This agency was superseded by the Office of Minerals Exploration (OME) on June 30, 1958. DMEA was authorized to contribute 75 percent of the allowable costs of the exploration specified in acceptable projects. With OME the contribution was reduced to 50 percent. Under DMEA, 209 contracts were approved in 16 States, and these totaled $6,505,111 in Government assistance. Only one project was approved under OME for $46,725 in Government assistance. By the end of 1963 $1,364,785 had been repaid on the loans.

PRICES

AEC encouraged the growth of the uranium industry by incentives which included bonuses and guaranteed prices for ores of various grades. The last price schedule, known as Circular 5, was issued in March 1951 and expired on March 31, 1962. After this date AEC contracted with mills for concentrates, and the mills purchased part of their ore supply on an open market basis. Nevertheless, the old Circular 5 prices continued to form the basis of ore purchases. Circular 5 stipulated a base price ranging from $1.50 per pound of U_3O_8 on ore grade of 0.10 percent to $3.50 per pound on ore containing 0.20 percent U_3O_8 or better. In addition premiums were allowed for ores over 0.25 percent, and a development allowance was paid on all ores. Thus, ores containing 0.15, 0.20, 0.25, and 0.50 percent U_3O_8 aggregated $3.00, $4.00, $4.15, and $4.45 per pound of U_3O_8. In 1962 and 1963, average price for ore, which averaged about 0.25 percent U_3O_8, was $4.05 per pound of contained U_3O_8. Under present contracts, mills are paid $8 per pound for specification-grade concentrates.

After 1968 concentrates will be purchased by AEC on the basis of 85 percent of audited allowable 1963–68 production costs per pound of U_3O_8 plus $1.60, but not to exceed a maximum price of $6.70.

Natural uranium metal has been quoted at $24 per pound for several years. Depleted uranium, in the form of UF_6, varied from $2.50 per kilogram of contained metal for material containing less than 0.38 percent U^{235} to $22.60 per kilogram for uranium containing 0.7 percent U^{235}.

Base charges for enriched uranium in the form of uranium hexafluoride (UF_6) varied with the degree of enrichment from $4.77 per gram of U^{235} content for 0.010 weight-fraction (1.0 percent) to $9.59 per gram for 0.050 weight-fraction and $12.01 for 0.90 weight-fraction material.

Base charges established by AEC for plutonium and for uranium enriched in the fissionable isotope U^{233} were—$43 per gram of contained Pu^{239} and Pu^{241}, the isotopes readily fissionable by thermal neutrons; and $82 per gram of contained U^{233}, subject to adjustment for the presence of other uranium isotopes. These charges apply to material distributed within the United States for research and medical therapy and to nations having cooperative agreements with the United States. They determine the payments due AEC for use, consumption, and loss of leased material, as well as sales prices for material sold.

Reduced base charges were established for these materials for use in certain research and development activities under domestic lease agreements. These charges are equal to estimated fuel values in thermal power reactors and were $10 per gram of Pu^{239} and Pu^{241} and $14 per gram of U^{233}, subject to adjustment for the presence of other uranium isotopes.

Prices on radioisotopes produced by AEC are listed in a Radio and Stable Isotopes Catalogue published by Isotopes Development Center at Oak Ridge National Laboratory, Oak Ridge, Tenn. Cobalt 60, the most widely used radioisotope, ranged from $2 per curie for specific activity of 1 through 25 curies per gram to $7.20 per curie for that having specific activity of 191 through 205 activities per gram. Discounts are made for quantities above 5,000 curies.

TAXES

The mining of uranium from domestic or foreign deposits is eligible for a 23-percent depletion allowance under the Internal Revenue Code of 1954.

TRANSPORTATION

Transportation of radioactive materials in interstate commerce by land or water is subject to Interstate Commerce Commission regulations. In aircraft, transportation of such material is regulated and prescribed by the Federal Aviation Agency. Pertinent regulations are also promulgated by the Coast Guard, and Post Office authorities. Detailed information on many of the basic problems involved in the transportation of radioactive material is contained in a preliminary report 2–5, Physical, Biological, and Administrative Problems Associated with the Transportation of Radioactive Substances, published by the National Research Council, Washington, D.C.

RESEARCH

Nuclear energy inspired worldwide research on a scale that was never before known. The Atomic Energy Act of 1954 directed AEC to promote the conduct of research and development—both within Government-owned facilities and by private and public organizations—that will assist in acquiring theoretical and practical knowledge about nuclear energy and its application. Research is conducted in Government-owned facilities and under contract with private and public organizations, such as colleges, universities, medical centers, and industrial firms. All phases of research are covered—basic, applied, and exploratory development.

Primary objective of AEC-sponsored research and development is to attain new knowledge about the nature of nuclear forces and their effects and how to put these effects to use for the good of mankind. Annual reports of this research are published and a listing of projects covered in the table of contents for 1963, occupied 13 printed pages (*17*). Broadly speaking, the type of research may be divided into five groups: (1) research in the medical and life sciences; (2) environmental radiation studies in ecology on land, fresh-water, and marine systems; (3) Plowshare program and fundamental science of nuclear detonations; (4) basic physical research in physics, nuclear physics, mathematics, chemistry, metallurgy, and controlled thermonuclear science; and (5) nuclear reactor research and development, including fuels, materials, reactor-component development, reactor physics, and chemical process development.

The 12 principal research and development installations of AEC (contractors are shown in parentheses) are as follows:

1. Ames Laboratory (Iowa State University), Ames, Iowa.
2. Argonne National Laboratory (University of Chicago), Lemont, Ill.
3. Bettis Atomic Power Laboratory (Westinghouse Electric Corp.), Pittsburgh, Pa.
4. Brookhaven National Laboratory (Associated Universities, Inc.), Upton, N.Y.
5. Hanford Laboratories (Battelle Memorial Institute), Richland, Wash.
6. Knolls Atomic Power Laboratory (General Electric Co.), Schenectady, N.Y.
7. Los Alamos Science Laboratory (University of California), Los Alamos, N. Mex.
8. Mound Laboratory (Monsanto Research Corp.), Miamisburg, Ohio.
9. National Reactor Testing Station (Phillips Petroleum Co., Aerojet General Corp., and General Electric Co.), Idaho Falls, Idaho.
10. Oak Ridge National Laboratory (Union Carbide Corp.), Oak Ridge, Tenn.
11. Sandia Laboratory (Sandia Corp.), Albuquerque, N. Mex.
12. University of California, E. O. Lawrence Radiation Laboratory (University of California), Berkeley and Livermore, Calif.

Other AEC research was conducted in 1963 under about 1,380 contracts, 668 were in biology and medicine, 568 were in physical research, and 144 were in reactor development and waste management. Table 11 lists AEC research and development costs for fiscal years 1959 to 1963. For comparison, the net cost of all AEC operations is included. AEC investment to June 30, 1963, for research and development totaled $1,886 million acquisition cost or a net after depreciation of $1,388 million. Comparative investment in production facilities was $5,447 million and $3,706 million, respectively.

For all practical purposes, most of this research is brought to fruition in the AEC Reactor Development Program, which was established in 1948 as a strictly governmental effort; the law then prohibited private ownership of any facilities capable of producing significant quantities of fissionable materials. In 1951, AEC invited private industry, at its own expense, to study reactors. The Atomic Energy Act of 1954 encouraged private initiative to enter into nuclear power development, and the first invitation issued in December 1953 led to the Shippingport Atomic Power Station. In 1955, AEC announced its Power Demonstration Reactor (PRD) Program which offered to assist in defraying the research and development costs of nuclear power reactors and to waive the use-charge for leased fuel during

TABLE 11.—*AEC research and development costs for fiscal years*

[Thousand dollars]

	1959	1960	1961	1962	1963
Development of nuclear reactors:					
Civilian nuclear power development	$105,233	$100,095	$102,305	$94,320	$88,140
Naval propulsion	90,614	88,799	93,442	95,375	108,889
Aircraft propulsion	71,822	69,687	71,116	(1)	(1)
Army reactors	9,376	11,945	13,532	12,844	11,583
Missile propulsion	22,820	31,777	23,080	21,466	25,291
Space propulsion	(2)	(2)	25,143	42,455	69,676
Auxiliary power sources	7,696	11,480	21,316	53,572	75,188
Merchant ships	4,737	4,165	5,341	9,045	7,450
General research and development	43,302	81,304	81,999	104,073	121,126
Total	355,600	399,252	437,274	433,150	507,343
Research:					
Physical research	112,318	132,845	154,105	171,782	198,526
Biology and medical research	42,781	48,878	53,866	62,782	70,523
Peaceful application of nuclear explosives	2,486	6,392	7,311	9,329	11,002
Isotope development	2,077	3,808	3,655	6,306	6,815
Total	159,662	191,923	218,937	250,199	286,866
Net cost of all AEC operations including depreciation	2,496,648	2,619,143	2,615,764	2,695,936	2,713,207

[1] The Aircraft Nuclear Propulsion program was terminated in 1961.
[2] Included with missile propulsion.

Source: AEC annual financial reports for 1960–63.

early years of the plant operation. Since 1955, AEC has invested about $3.5 billion in the development of nuclear reactors and has also engaged in a series of cooperative agreements with industry for civilian power development (*11*).

The first invitation of the PDR Program, issued in January 1955, offered technical and financial assistance including the waiver of normal charges for special nuclear materials and the support of research and development. From this the Yankee Atomic Power Plant, the Hallam Nuclear Power Facility, and the Enrico Fermi Atomic Power Station (see table 3) were undertaken.

The second invitation, issued in September 1955, requested proposals for small-scale nuclear power plants in which AEC owns the nuclear steam supply system and paid the cost of fabricating the first core as well as related research and development costs. The utility provides plant site, furnishes the nonnuclear power facilities, operates the nuclear portion under contract with AEC, purchases from AEC the steam produced by the reactor, and has an option to purchase the reactor. Under this arrangement, the Piqua and Elk River reactors were constructed.

The third invitation extended in 1957 was in most respects similar to the first invitation, but placed no limit on the type or size of plant. This led to the planning of the Carolinas-Virginia and Pathfinder reactors. A modification of the invitation led to the planning of the Malibu and Haddam Neck plants. The Peach Bottom reactor, using uranium-thorium fuel was in response to a separate invitation.

Unsolicited proposals from industry for cooperative nuclear power-plant projects were included in AEC 1960 authorization acts and led to the construction of the Big Rock, Puente Higuera, LaCrosse, and San Onofre nuclear prototype plants.

The Dresden, Indian Point, Humboldt, Oyster Creek, and Nine Mile Point reactors were initiated by utility companies without AEC assistance.

Early in 1964, AEC invited electric utilities to submit proposals for the design, construction, and operation, in cooperation with the Government, of a number of prototype advanced converter reactor plants. Two proposals were accepted as a basis for seeking authorization and funding. One was for a 260,000-kilowatt high-temperature gas-cooled reactor proposed by Rochester Gas & Electric Corp. and General Dynamics Corp., to be built near Rochester, N.Y. The other was for a 525,000-kilowatt seed-blanket reactor employing the thorium fuel cycle. This was proposed by the California Department of Water Resources and, if located on the coast, the plant may include a sea-water desalting facility.

Most companies interested in nuclear developments also maintain research and development facilities at their own expense, some of which are very large. It would be impossible to cover even a token reference to research activities in this chapter, as the annual AEC reports of some 400 pages profess only to be able to cover the highlights of their research activities. The results of most research activities, except for secret and proprietary information, is published in technical journals. AEC publishes abstracts of the international literature on nuclear science and technology issued twice each month since 1947 as Nuclear Science Abstracts (*16*).

Basic research has lead to the development of more versatile, efficient, and economic ore treatment and chemical separation methods. Techniques, such as ion exchange and solvent extraction used mostly on a laboratory scale before 1950, came into wide use in large-scale plant operations. The Bureau carried out an extensive program of ore-sample analysis, process development, and ore-amenability testing under a cooperative arrangement with AEC. The Bureau also worked with the Battelle Memorial Institute and Rohm & Hass Laboratories in developing amine extractants. The Bureau has contributed to reactor development and waste management in such widely diversified fields as metal-melting research, alloy development, thermodynamics, high-temperature heat transfer, and application of gas bearings to turbocompressors. Metallurgical work has extended to other metals, such as zirconium, columbium, hafnium, and rare-earth metals, which have specialized applications in reactors.

OUTLOOK

Uranium production probably will lag appreciably behind the general metal industry and national rate of growth until 1970 or 1980. After that the adoption of nuclear power is expected to accelerate, overtaking the national growth trend and possibly reaching boom proportions. Nuclear weapons will continue to be the major factor in requirements over the next decade. Uranium requirements for nuclear power plants between now and 1966 will total only a few thousand tons. The AEC estimates of domestic civilian uranium requirements range from 1,600 to 4,000 tons of U_3O_8 per year in 1970, 8,900 to 14,000 tons in 1975, and 19,000 to 27,000 tons in 1980. Foreign requirements for uranium enriched in AEC facilities might be of the same magnitude.

The short-term outlook for mine and mill production of uranium oxide (U_3O_8) is closely circumscribed by AEC procurement contracts which extend through 1966 in most cases and through 1970 in some cases. Domestic procurement as planned by AEC will gradually decrease from the 17,000 tons of U_3O_8 produced annually in 1960–62 to 7,800 tons in 1968–70. Procurement from foreign sources, which was higher up to 1960 than domestic production, will decrease rapidly and cease after 1967.

Development of peaceful uses for nuclear explosives is the objective of the AEC Plowshare program in which the Bureau cooperates. Civil works applications under consideration include excavation of harbors, canals, highway and railroad cuts, and other similar works; mining applications being studied include stripping of overburden prior to open pit mining, breaking of ore underground for mining by methods similar to block caving, and fracturing of low-grade ore deposits for in-situ leaching; petroleum applications include fracturing of low permeable gas and oil beds to stimulate products movement, fracturing of oil-shale for in-situ retorting, and recovery of oil from tar sands. Production of chemicals and radioisotopes on a large scale in underground formations appears possible and preliminary results of tests are favorable. Plowshare activities include research to develop nuclear devices for special application where very low radioactivity is required or where high neutron flux is required. Studies of product contamination and methods to prevent contamination or to decontaminate such products are being made.

The present AEC contract price of $8 per pound of U_3O_8 in concentrate form will remain in effect until 1969 when the price will be limited to a maximum of $6.70 per pound. World prices then are expected to stabilize probably around $5 per pound of U_3O_8 until such time that demand begins to approach production ability.

Legislation enacted in 1964 amended the Atomic Energy Act of 1954 to permit full private ownership of special nuclear materials and eliminated mandatory Government ownership. One of the principal effects of this legislation will be the establishment of open-market prices for all nuclear materials based on fuel value rather than weapon value or military exigency. After 1970, when the present procurement contracts expire, the industry will be ruled by the same economics of supply and demand as any other mineral commodity. Domestic producers may be faced with strong foreign competition.

Aside from nuclear weapons, uranium will continue to be used mainly for nuclear applications, the principal ones being heat and power reactors, both civilian and military, including naval propulsion. The world has such need for power sources that the incredible energy of nuclear fission is already at work in many countries around the globe. The only indeterminate factor is the future date at which nuclear power will be ready for general acceptance and begin its ascendency. Long-term projections on the demand for uranium depend on an evaluation of the trends of basic research and development both in reactor technology and in power production from fossil fuels. Since progress is dynamic in all these fields, forecasting is exceedingly difficult, and continuous study and revaluation will be required for the guidance of industry. Nuclear power development has

proceeded rapidly, and the imminence of economic nuclear power has stimulated the coal and coal-transport industries to greater efficiencies. For some time yet to come, nuclear power plants will be justified only in locations where fossil fuel costs are high. A faster rate of nuclear power development will probably take place in Great Britain than in the United States, because the English coal measures are declining in productivity and coal prices are rising. On the other hand, unpredictable discoveries of large pools of oil or gas can upset the best of calculations. Typical of this is the recent discovery of natural gas in Holland, which apparently will provide low-cost fuel in that area for many years.

Nonnuclear applications of depleted uranium are being developed and will provide a small supplemental market. Research in this field has been intensive, both in this country and abroad, and has produced many prospective useful applications.

The utilization of radioisotopes will continue to increase as new applications are found and old ones are broadened. Radioisotope production in special reactors will decline as the reprocessing of nuclear fuel from power reactors increases, when the supply of many of the long-lived isotopes will be far in excess of demand.

The U.S. Government, as well as many other governments, will continue to assist in the research and development of nuclear energy for both peaceful and military uses. The long-term plans of AEC include an extensive nuclear-reactor research and development program predominantly concerned with advanced nuclear systems, developing and improving nuclear power and propulsion systems, and improving engineering safeguards for all nuclear applications. Reactor development includes cooperative assistance in constructing plants, utilizing presently most competitive reactor types and the development, construction, and demonstration of advanced converter and breeder reactors which will fill the long-range needs of utilizing fertile as well as fissile fuels. The advanced types of reactors on which development can be expected include those moderated with heavy-water, the sodium-cooled graphite-moderated type, the gas-cooled high-temperature reactor, the seed-blanket type, and the nuclear superheat concept, all of which are classed as converter reactors that produce almost as much fissionable material as they consume in their operation. Breeder types, that produce more fissionable material than they consume, also will continue to be investigated intensely in a long-range effort to develop the utilization of the full potential energy available in nuclear fuels.

AEC will also continue its other major activities including basic research in physics, biology, and medicine; the applications of nuclear explosives to excavation and mining (Plowshare program); the application of nuclear energy to the desalination of water; the development of radioisotopes; and its support activities which include educational assistance, industrial relations, public and technical information programs, and, of course, the regulatory activities of licensing, compliance, and radiation protection.

The use of uranium will not suffer materially from competition by thorium breeder reactors. Thorium reactors offer certain theoretical advantages, but they also have many disadvantages that must be overcome by research and development. It is probable that both uranium and thorium will find specific applications and, in the distant future, will complement each other. In any case, fissionable U^{235} will be required to initiate and maintain a thorium breeder until such time (probably around 10 years) that sufficient U^{233} has been produced to replace the U^{235}.

Thermonuclear energy produced by the nuclear fusion of the light nuclei deuterium and tritium does not appear to threaten the uranium industry, barring some senational unpredictable discovery. While fusion has been accomplished on a very small scale, many difficult problems must be solved to arrive at its practical application, and for some of these a means of approach have not been developed.

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PROBLEMS

The uranium industry has the problem of adjusting to a very low level of activity until market growth resumes, possibly after 1970. Producers also face the necessity of making a transition and adjustment from a guaranteed market to a free market. Planning is difficult because demand, prices, and the nature of foreign competition are difficult to assess with any degree of certainty.

Relatively little exploration has been done in the major uranium-producing countries since 1958, and production has depended largely on reserves developed in the 1950's and has depleted and probably will continue to deplete known reserves for some time. Many experts believe that nuclear-power developments will surge ahead rapidly by 1970 or 1980. Since new reactors require a large initial charge of uranium, an extensive program of reactor building could exhaust reserves rapidly and result in a shortage. There need be no concern about a shortage if exploration is undertaken well in advance of the expanding requirements.

The extremely varied aspects, attitudes, and distribution of uranium ore deposits present many mining problems. Likewise, complex mineralogical associations pose metallurgical problems. Constant research and development in these areas will be necessary for those who wish to stay in business in the face of competition, rising costs, and lower grade and deeper ores. Mining of incompetent ground, control of ground water, and combating the hazard of radioactivity, particularly from radon, are major factors that tend to increase mining costs. Means of simplifying or improving ore processing as applied to increasingly more complex lower-grade ores will be essential to maintaining an adequate supply and a stable industry.

Uranium ores contain many potential by-products, including vanadium, molybdenum, selenium, scandium, and radium, some of which are incompletely recovered or not recovered at all. Economic methods of recovery need to be studied to recover and conserve these elements.

Acquiring comprehensive knowledge on the application of nuclear explosives to mining and excavation present a broad field for research and investigation.

Problems associated with the application of nuclear energy and radiation involve almost every scientific and engineering discipline and range from basic or fundamental principles to the practical design, construction, and operation of reactors. Even those involving nuclear reactor research and development are too numerous to list herein. Those of primary interest to the mineral industry include the study and improvement of reactor components, particularly fuels and fertile materials, fuel reprocessing, and cladding and structural materials. A major problem is the development of structural reactor components suitable for operating above 2,000° C.

Reactor accidents can result in serious explosions or in release of fission products, either of which can create radioactivity hazard over a wide area. The safety record with reactors has been excellent, largely because of the safety measures employed. Engineering design must include multiple precautions against any conceivable eventuality. At the same time, the public, often confused by publicity regarding fallout from nuclear explosions, must be kept informed of these safeguards; otherwise suspicion and fear can create serious problems in choosing sites for nuclear reactors.

The disposal of radioactive waste poses problems in all operations from the mining and milling of uranium ores to its refining and the fabrication of fuel elements. However, fission products contained in irradiated fuel elements constitute the dominant waste disposal problem. Present methods of disposal consist mainly of deep burial, either in the sea or underground, of variously compounded forms containing the radioactive materials. Some more useful method should be devised, and one of the more favorable avenues of attack would be to develop methods of utilizing either the heat or radiation being generated by these wastes.

Large stocks of depleted uranium, mainly uranium 238 from which most of the fissionable uranium 235 has been separated, have been accumulated. Means of utilizing this depleted uranium are urgently needed.

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VANADIUM

By Gilbert L. DeHuff [1]

VANADIUM is an important alloying element in steels and other metals and an important catalyst for various industrial processes including sulfuric acid production and petroleum refining.

For more than two decades the United States has been the largest producer of vanadium with most of its production coming from the Colorado Plateau area in association with the production of uranium. The Republic of South Africa and the U.S.S.R., both with very large vanadium resources, are becoming important producers. U.S. reserves of high-grade material are limited, but relatively low-grade resources are large. The principal domestic resources are contained in the vanadiferous shales and phosphate rock of the Phosphoria formation in Idaho.

The chief use of vanadium is as an alloying agent for steels and irons, usually in small quantities and in company with other alloying elements. In this connection it is used to reduce and control grain size; to impart toughness, strength, and resistance to impact and abrasion; and to maintain hardness at increased temperatures. Furthermore, it is an important constituent of titanium and aluminum alloys. It has numerous chemical uses, one of the most important being in the preparation of catalysts for various industrial processes including the production of sulfuric acid.

Consumption of vanadium is growing rapidly. With decline in production from Colorado Plateau ores, the United States will need to turn more toward other sources for its vanadium. It will need more economical methods for recovery of the vanadium from large low-grade resources if it is to meet the demand without depending on foreign sources.

BACKGROUND

Vanadium was identified as a distinct element about 1830, and its salts had found uses by 1860 in coloring fabrics, leather, glass, and pottery. Its employment as an alloying element in steels was recognized by the U.S. automobile industry by 1905 and was advertised as a feature of the 1908 Ford. In 1896, French scientists had experimented with vanadium as an alloying agent in armorplate, and work at Sheffield, England, in the following years determined that it improved cutlery, tools, and constructional steels as well as armor.

Some vanadium-uranium ores were mined in Colorado as early as 1902, but discovery of the rich Peruvian deposit of Mina Ragra in 1905 appears to have launched the vanadium industry in the United States on a significant scale.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

For more than 20 years the United States has been the largest producer and apparently the largest consumer of vanadium, but production has decreased since stretchout of the Atomic Energy Commission's (AEC) buying program for uranium. The great bulk of the Nation's production in recent years has been as a coproduct or byproduct of uranium mining and processing operations, and more vanadium has been available from these mined ores than could be used or exported. This has resulted in some accumulation of intermediate sludges, tailings, and other materials which have had the uranium removed but not the vanadium. Although this vanadium production has been dependent

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on uranium production, a substantial quantity of uranium has been produced during this period from ores too low in vanadium to warrant treatment for its recovery. Before becoming dependent on uranium output a large portion, perhaps more than half, of U.S. production of vanadium was from Colorado Plateau ores which were of relatively low uranium content—too low, for the most part, to be of continued interest when the uranium market developed.

At the end of 1963, four companies (table 1) were operating one mill each to recover vanadium in the form of vanadium pentoxide from western uranium-vanadium ores, which were obtained both from company mines and from independent operators. Two of these companies also were producing ferrovanadium, but each at locations other than their oxide mills. Two other companies were significant producers of ferrovanadium. In all cases, production of ferrovanadium was accomplished in plants producing other ferroalloys as well. Several firms recovered relatively small quantities of vanadium pentoxide or ammonium metavanadate from miscellaneous sources such as ferrophosphorus, foreign chrome ores, and oil residues.

TABLE 1.—*Principal producers of vanadium oxide and ferrovanadium in the United States, in 1963*

Company	Location	Product
American Metal Climax, Inc.	Grand Junction, Colo.	Oxide.
Mines Development, Inc.	Edgemont, S. Dak.	Do.
Reading Alloys Co., Inc.	Robesonia, Pa.	Ferrovanadium.
Shieldalloy Corp.	Newfield, N.J.	Do.
Union Carbide Corp., Metals Division.	Alloy, W. Va.	Do.
Union Carbide Corp., Nuclear Division.	Rifle, Colo.	Oxide.
Vanadium Corp. of America.	Cambridge, Ohio	Ferrovanadium.
Do.	Shiprock, N. Mex.	Oxide.

The European market is supplied by vanadium pentoxide from Finland, South-West Africa, the Republic of South Africa, and the United States. Extensive iron ore deposits having a vanadium pentoxide (V_2O_5) content of 0.02 to 0.20 percent, occurring in Germany, France, Luxembourg, and Belgium, provided vanadium for Germany in World War II. Vanadium was also obtained by Germany at that time from Swedish and Norwegian iron ores and from steel mill slags. These slags, bauxite residues, and iron ores possibly still contribute some vanadium to the European supply.

The Finnish production comes from vanadiferous, titaniferous magnetite of the Otanmäki mine at Otanmäki in central Finland. The Otanmäki company is a wholly government-owned corporation.

South-West African shipments are obtained from oxidized ore of the upper levels of the Berg Aukas lead-zinc mine of South West Africa Co., Ltd.

Transvaal Vanadium Co. (Pty.) Ltd., a subsidiary of Anglo American Corp., was the only producer in the Republic of South Africa in 1963. However, another subsidiary of Anglo American Corp., Highveld Development Co., Ltd., was seriously investigating the possibilities for a steelmaking project which would produce 12,500 short tons of coproduct vanadium pentoxide annually. African Metals Corp., Ltd., also was engaged in exploratory work in 1963 looking to possible production of vanadium pentoxide for export.

The U.S.S.R. appears to have satisfied its needs for vanadium, at least in part, from small vanadate deposits and from certain vanadiferous iron ores. Plans for increasing regional steel production, using iron ore from large vanadiferous deposits which until now have been relatively untapped, are expected to result in a big increase in vanadium production.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Technical-grade vanadium pentoxide is the most common product of the vanadium mills and is the feed material generally used for production of ferrovanadium, other vanadium alloys, and metal. It also has chemical uses. Relatively small quantities are used for direct additions to electric-furnace steels. It is available as the fused oxide (flakes generally containing 86 to 99 percent V_2O_5), also called black flake, fused black oxide, and black oxide, or even loosely referred to as vanadic acid; or it may be obtained as air-dried oxide (a powder analyzing 83 to 86 percent V_2O_5). National Stockpile Specification P–58–R, December 11, 1957, "Vanadium," specified that grade A fused black vanadium oxide procured for the national stockpile shall have a minimum V_2O_5 content (dry basis) of 86.00 percent. The maximum limits for eight elements other than vanadium or oxygen were each set at 0.15 percent or less, and for insolubles at 1.00 percent.

Chemical grades of vanadium pentoxide, variously referred to as high-purity, purified, or C.P. yellow air-dried, have typical V_2O_5 contents of 99.5, 99.7, and 99.94 percent, respectively.

Ammonium metavanadate (NH_4VO_3), another form in which vanadium is marketed, particularly appeals to the chemical industry's requirement for vanadium. It is available commercially in both technical and chemically pure grades. Other oxides include sodium

metavanadate, sodium orthovanadate, and red cake (sodium polyvanadate). The latter is the mill-product oxide immediately before the final step of fusing to obtain the technical-grade pentoxide product.

Ferrovanadium, an alloy of iron and vanadium, is marketed in a number of grades. Those for use in steelmaking are the large-volume items. They consist of the open-hearth grades, containing 50 to 57 percent vanadium, with maximums of 8 percent silicon and 1 to 3 percent carbon; the crucible or special grades, containing 50 to 57 or 70 to 80 percent vanadium, with maximums of 2.25 percent silicon and 0.50 percent carbon; and the refined, primos, or high-speed grades, containing 50 to 57 or 70 to 80 percent vanadium, with maximums of 0.50 to 1.50 percent silicon and 0.20 percent carbon. Foundry-grade ferrovanadiums are available with 38 to 42 percent vanadium, 7 to 11 percent silicon, and 1 percent carbon; or with 50 to 55 percent vanadium, 10 percent silicon, and a maximum of 3 percent carbon.

Vanadium metal is produced as a 90-percent grade, used for alloying purposes, or as a high-purity, ductile metal containing 99.5 percent or more vanadium. The latter can be obtained as crushed material, as ingot metal, or as wire, rod, sheet, foil, and other fabricated forms.

TECHNOLOGY

Geology

Among the more important of the discrete vanadium ore minerals have been the complex sulfide, patronite; the vanadium mica, roscoelite; the hydrous potassium uranium vanadate, carnotite; and the lead vanadates, vanadinite and descloizite.

The most productive source of vanadium in the past 20 years has been the uranium-vanadium deposits in the sandstones of the Colorado Plateau. They have consisted for the most part of numerous, widely distributed, relatively small, tabular deposits; carnotite and roscoelite have carried much of their vanadium content.

At Mina Ragra, in the Andes of Peru at 16,500 feet, a lens-shaped body of asphaltite and patronite, dipping 75° and occupying a fracture in shales and thin-bedded limestone of Cretaceous age, was mined for its vanadium content from 1907 until August 1955. A variety of vanadates, together with vanadium sulfate, occurred as alteration products in the oxidized zone near the surface (*6*).[2] Other similar asphaltic veins are found in the same sedimentary beds of the region but contain only about 1 percent V_2O_5—a much lower vanadium content. Vanadiferous asphalts also are known in other countries (*4*).

Vanadates of lead, zinc, and copper found in the oxidized portions of certain base metal deposits have been the source of the vanadium produced in South-West Africa and Northern Rhodesia. Minor production has come from the Southwestern United States and from Mexico. Other occurrences have been reported from Spain, Africa, and Australia.

Vanadium is a constituent of many iron deposits, vanadium ions replacing those of iron in iron and other minerals rather than occurring as distinct, identifiable, vanadium minerals. Vanadiferous titaniferous magnetites in South Africa and Finland have become important sources of vanadium, and large deposits are known in the U.S.S.R. and the United States. Although these magnetites are associated with both anorthosites and gabbros, the most promising for vanadium are those associated with the anorthosites. The vanadium is linked principally to the magnetite rather than the ilmenite mineralization of these bodies. Vanadium is also a constituent of some sedimentary iron ores to the extent that they can be considered a source, or potential source, of vanadium. Deposits of this kind are under development in the U.S.S.R.

Vanadium occurs as a constituent of certain clays and shales. The vanadium content usually increases with increase in the content of organic material, and certain phosphatic shales and phosphate rock of the Phosphoria formation of Idaho and Wyoming represent a large resource. Some coals also contain sufficient vanadium to yield several percent vanadium in the ash; others are virtually without vanadium. Certain petroleums, particularly in Venezuela and Mexico, have sufficiently high vanadium content to justify its recovery from the oil's residues and soots.

Some bauxites and laterites contain vanadium, as do some titaniferous magnetite beach sands. Although the vanadium content of most bauxite is low, in certain European countries vanadium is sufficiently concentrated in the red muds of the Bayer-alumina process to warrant its recovery.

Mining

Prior to 1948 Colorado Plateau ores were mined underground at shallow depths, on a highly selective basis, and on a small scale. The small pods or lenses which constituted the ore being mined were developed by adits or inclines, and there was little mechanization. Since emphasis has shifted to large-scale uranium production, large low-grade deposits have yielded

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

the bulk of the ore; some contain commercially recoverable vanadium and some do not. Mining is by both open pit and underground open stope or room-and-pillar methods. Vertical shafts as deep as 600 feet have been employed to reach the deeper bodies not outcropping in canyon or rim rock walls.

Vanadium mining in Peru has been both by open cuts and underground from adits.

Metallurgy

Before 1948 recovery of vanadium from carnotite and roscoelite ores employed a salt roast from 825° to 850° C to produce sodium vanadate soluble in water or in a sodium carbonate solution. After adjusting the pH of the leach solution with acid, red cake (sodium polyvanadate) was precipitated, which upon filtering, washing, and subjecting to a direct flame, yielded the fused vanadium pentoxide product containing approximately 86 percent V_2O_5 (*2*).

With development of the demand for uranium, milling was altered by the addition of circuits to provide for recovery of that element. Uranium recovery soon became the controlling factor in mill design with vanadium recovery assuming a subordinate position. Flowsheets for the mills treating western uranium-vanadium ores have become more complex with variations in the leaching processes and adoption of solvent extraction or ion exchange procedures.

Finland pioneered in the commercial recovery of vanadium from vanadiferous titaniferous magnetite. As originally processed in 1956, a magnetite concentrate was obtained which was cleaned, dried, and mixed with sodium salt for pelletizing in a round-shaft furnace designed to promote reaction between the sodium and the vanadium contained in the magnetite. By countercurrent leaching of the pellets with hot water, a pregnant leach liquor was obtained containing the vanadium as sodium vanadate, while the leached pellets constituted a high-grade iron concentrate product. The pregnant solution was treated with sulfuric acid to precipitate the vanadium as vanadic acid, which was recovered from the solution by pressure filters, cleaned of impurities, smelted, and cast into cakes containing 90 to 92 percent V_2O_5 (*2*).

Ferrovanadium is the principal form in which vanadium is used by the steel industry. The alloy is produced by reduction, utilizing a thermic process or an electric furnace. Reduction may be accomplished with silicon, aluminum, or carbon; the type of reductant and method used are affected by the grade of ferrovanadium to be produced. A typical charge for an electric furnace, using carbon as the reductant, might consist of technical-grade vanadium pentoxide, or less commonly some other form of vanadium-bearing material such as slag, ore, or concentrate; steel scrap, coke, and fluxes would make up the balance of the charge. When aluminum is the reductant, an exothermic reaction takes place and no carbon is required in the charge. Ferrosilicon may be used for reduction of the vanadium pentoxide in a two-stage process employing lime and fluorspar in a magnesite-lined furnace. Carbon, although the least expensive, is least satisfactory of the reductants (*2*).

Vanadium metal of 90 percent purity, used for alloying purposes where low-iron or other low-impurity features are desired, is produced commercially by the aluminothermic process; high-purity, ductile vanadium metal is produced by bomb reduction of vanadium pentoxide with calcium.

USES

Small quantities of vanadium added to steels and irons impart beneficial qualities to the product. Vanadium's chief functions are to reduce and control grain size (*14*) and to provide various other alloying effects. Among the benefits achieved are—toughness, strength, improved machinability and weldability, reduced distortion, simpler heat treatment, increased wear and impact resistance, uniformity, better finish, reduction of flaking of carburized surfaces, and ability to maintain high hardness to nearly 1,200° F (*11*). Tool steels, engineering and constructional steels in both light and heavy sections, heat-resistant stainless steels, spring steels, steel and iron castings, steel mill rolls, nonaging rimming steels, and nitriding steels are among the beneficiaries. As an alloying agent for steels and irons, vanadium usually accompanies other alloying elements rather than being used alone (*3*).

Vanadium is employed as an alloying agent in nonferrous alloys, chiefly those of aluminum and titanium, to control thermal expansion, grain size, and electrical resistivity and to improve high-temperature strength. Titanium-base vanadium alloys, having high-temperature strength qualities and good weldability, have become of interest to the aerospace industry. Vanadium is a constituent of permanent magnet alloys and of welding rods and coatings, and it is of interest as a structural material for nuclear reactors.

Compounds of vanadium are important to the chemical industry as catalysts for many industrial processes, including the production of sulfuric acid and the cracking of petroleum. Other chemical applications include use as coloring in glass and ceramic glazes, as driers in paints and varnishes, and in the processing of colored film (*2*).

ALTERNATE MATERIALS

Chromium-vanadium steels have been substituted for nickel-bearing steels. Manganese-titanium steels and molybdenum or molybdenum-silicon steels with a grain-refining addition of aluminum have served as substitutes for vanadium steels. For many of its alloying purposes vanadium is interchangeable to some extent with other alloying elements such as molybdenum, tungsten, and columbium. Platinum can substitute for vanadium compounds as a catalyst.

RESERVES AND RESOURCES

Both free world and Communist nation resources of vanadium are large, and an appreciable part of these resources may be considered in the reserve class when coproducts become part of the scheme of exploitation. The United States does not now have long-range self-sufficiency in coproduct vanadium reserves, but its resources are large.

Owing to the extensive mining stimulated by the AEC buying program of the fifties and sixties, the known vanadiferous uranium ores of the Colorado Plateau cannot be relied upon as a substantial reserve after 1970. Other vanadium reserves of the United States lie in those vanadium ores of the Colorado Plateau that are low in uranium content and in the byproduct vanadium to be obtained from the vanadiferous phosphate rock of Idaho (*4*).

The Colorado Plateau deposits low in uranium content were mined for vanadium before the great demand for atomic energy materials focused attention on other deposits of the Plateau. The ore of the low-uranium deposits, near Placerville, Rico, and Rifle, Colo., contains 1.5 to 2.0 percent V_2O_5 (0.8 to 1.1 percent vanadium) with a developed reserve reported in 1961 as approximately 500,000 tons of ore, or 10 million pounds of vanadium. The potential of these deposits as a resource, largely near Placerville, Colo., is probably several million tons of ore of comparable grade.

The vanadium-bearing phosphate rock of Idaho, containing 0.1 to 0.3 percent V_2O_5 (0.06 to 0.17 percent vanadium), represents a very large resource—conceivably measured in billions of pounds of vanadium. As a reserve, these deposits are dependent on the capacity to produce, and the demand for, phosphorus and its compounds.

The titaniferous magnetites of Lake Sanford, N.Y., and of Iron Mountain, Wyo., with a V_2O_5 content of 0.4 to 0.45 percent (0.2 to 0.25 percent vanadium), constitute other domestic vanadium resources. Other titaniferous magnetites, and vanadiferous phosphatic shales in Idaho and Wyoming of higher vanadium content than the rock now being mined for phosphates, also represent substantial resources of vanadium but have less attractive possibilities for the coproducts needed for favorable consideration of exploitation in a peacetime economy. In addition, vanadium of Colorado Plateau low-vanadium uranium deposits (roughly 0.07 percent vanadium) remains a significant resource, although not attractive for recovery under current conditions.

Large reserves of vanadium occur in the outcropping titaniferous magnetites of the Bushveld complex of the Republic of South Africa. These deposits have been estimated to average 1.8 percent V_2O_5 (1.0 percent vanadium) and to have at least 4 billion pounds of vanadium easily accessible at surface, or over 10 billion pounds to "reasonable mining depths" (*13*).

Titaniferous magnetites in Finland, containing approximately 0.25 percent vanadium, constitute a vanadium resource estimated to have from 150 million to 250 million pounds of vanadium content; the availability of the vanadium content is dependent on the demand for iron ore and titanium.

The U.S.S.R. has large reserves of vanadium which occur as a constituent of titaniferous magnetite at Kachkanar in the Urals and as a constituent of high-phosphorus brown ironstones in the Urals and at Kerch in the Crimea. Resources may be 13 billion pounds or more of recoverable vanadium. Active plans for development of these iron ores include recovery of the vanadium content as a coproduct, linked to steel production targets for 1965 and 1970 (*1*, *7*, *10*). Mainland China is reported to have reserves of vanadiferous titaniferous magnetite which are probably about 10 million tons of ore containing 0.15 to 0.3 percent vanadium.

SOURCES OF STATISTICAL INFORMATION

Statistics for domestic production and consumption of vanadium ores, concentrates, oxides, alloys, and metal are obtained on a voluntary reporting basis by periodic canvasses of the Bureau of Mines. U.S. import and export statistics are compiled by the Bureau of the Census from data filed by the importer or exporter with the Bureau of Customs. Data on foreign production are obtained by the Bureau of Mines largely from questionnaires sent to U.S. consular offices abroad, whose principal sources of information are the official statistical releases of the particular foreign governments concerned. This information is supplemented by data from other sources, including special State Department dispatches.

PRODUCTION, CONSUMPTION, AND TRADE

Table 2 shows mine production of vanadium in the United States as measured by receipts at the mills, and the recoverable vanadium that could have been obtained from those mill receipts if they had all been run through the mill. Recoverable vanadium may be defined as the quantity of vanadium that it is possible to extract from the ores (or concentrates) received at a mill, as calculated by using the recovery factor actually obtained by that mill from the ores (or concentrates) that it actually processed in the same year.

TABLE 2.—*Mine production and recoverable vanadium in ore and concentrate produced in the United States*

[Short tons]

Year	Mine production [1]	Recoverable vanadium
1954–58 (average)	6,022	3,380
1959	7,392	3,719
1960	8,047	4,971
1961	6,359	5,343
1962	7,647	5,211
1963	6,047	3,853

[1] Measured by receipts at mills, vanadium content.

Table 3 shows production of vanadium pentoxide in the United States from all sources, including that recovered from ferrophosphorus, oil residues, and imported chromium ores in the course of producing chromium chemicals.

TABLE 3.—*Production of vanadium pentoxide in the United States*

[Short tons]

Year	Gross weight	V_2O_5 content
1954–58 (average)	6,890	6,128
1959	7,906	7,305
1960	10,767	9,812
1961	10,796	10,387
1962	6,876	6,403
1963	7,347	6,959

Foreign production (short tons) of vanadium in ores and concentrates in 1963 was reported as follows: Republic of South Africa, 1,381; South-West Africa (recoverable vanadium), 1,134; and Finland (estimated), 617. In addition, the U.S.S.R. produced vanadium for its own use, and Argentina is believed to have continued to produce a small quantity.

U.S. consumption of vanadium materials is shown by type of material in table 4 and by end use in table 5.

TABLE 4.—*Vanadium consumed in the United States, by type of material*

[Short tons, vanadium content]

Material	1962		1963	
	Quantity	Percent of total	Quantity	Percent of total
Ferrovanadium	1,710	74	2,302	79
Oxide	165	7	135	5
Ammonium metavanadate	126	5	122	4
Other	313	14	347	12
Total	2,314	100	2,906	100

TABLE 5.—*Vanadium consumed in the United States, by end uses*

Use	1962		1963	
	Short tons	Percent of total	Short tons	Percent of total
Steel:				
High-speed	394	17	336	12
Hot-work tool	111	5	122	4
Other tool	75	3	94	3
Stainless	19	1	34	1
Other alloy [1]	1,103	48	1,573	54
Carbon	148	6	247	9
Gray and malleable castings	21	1	19	1
Nonferrous alloys [2]	235	10	299	10
Chemicals	163	7	139	5
Other [3]	45	2	43	1
Total	2,314	100	2,906	100

[1] Includes some vanadium used in high-speed or other tool steels not specified by reporting firms.
[2] Principally titanium-base alloys.
[3] Includes high-temperature alloys, welding rods, and cutting and wear-resistant materials.

TABLE 6.—*Exports of vanadium from the United States, by classes*

Year	Vanadium ore, concentrates, pentoxide, vanadic oxide, vanadium oxide, and vanadates (except chemically pure grade)		Ferrovanadium and other vanadium alloying materials containing over 6 percent vanadium		Vanadium-bearing flue dust and other waste materials	
	Short tons (vanadium content)	Value	Short tons (gross weight)	Value	Short tons (vanadium content)	Value
1954–58 (average)	589	$2,534,886	128	$539,026	27	$45,652
1959	1,240	4,667,764	152	529,697	42	40,317
1960	3,690	14,123,653	162	506,624	39	59,389
1961	2,081	7,659,955	120	436,208	92	29,077
1962	1,021	2,997,995	201	745,912	82	23,527
1963	536	1,641,122	183	587,690		

Source: Bureau of the Census.

Imports of vanadium into the United States halted in, or previous to, 1955. They had consisted of ore or concentrate from Peru; flue dust from Canada, Venezuela, Peru, and Curacao; and ferrovanadium from Japan, France, Germany, and the United Kingdom. Imports resumed on a small scale in 1959. Ferrovanadium imports became appreciable in 1962 (88 short tons), and in 1963 general imports of ferrovanadium totaled 481 short tons. Exports of vanadium from the United States are shown in table 6. The largest recipients of U.S. oxide in 1963, Japan and Belgium-Luxembourg, also were important suppliers of the U.S. imports of ferrovanadium in that year.

According to the Tariff Schedules of the United States, effective August 31, 1963 (U.S. Tariff Commission, TC Publication 112), vanadium ore and concentrate enter the United States duty free; for ferrovanadium, a rate of 12½ percent ad valorem applies to the product of most nations, and 25 percent ad valorem to that of the U.S.S.R., mainland China, and certain other specified Communist countries; for unwrought vanadium metal, the respective rates are 10 and 25 percent ad valorem.

STRATEGIC CONSIDERATIONS AND GOVERNMENT PROGRAMS

Vanadium is classified as a strategic and critical material and is held in the national stockpile. During the 10 year period of AEC uranium procurement, the domestic vanadium supply as a byproduct of uranium was so large that the United States became a net exporter. As this byproduct source declines the United States could become more dependent upon overseas vanadium sources. On June 30, 1964, government inventories in the national (strategic) stockpile totaled 7,865 tons.

PRICES

A price of 31 cents per pound of contained V_2O_5 continues to be quoted, nominally, for domestic vanadium ore. Quotations for technical-grade vanadium pentoxide, $1.15 per pound of contained V_2O_5, are for small quantities; actual prices for large lots dropped to about 80 cents per pound by the end of 1963. These had recovered to about 95 cents by the beginning of 1965. Between 1941 and 1959, the price for technical-grade vanadium pentoxide ranged from $1 to $1.38. It was quoted at $1.38 from 1959 through 1962.

Ferrovanadium prices increased from $2.70–$2.90 per pound of contained vanadium in 1940 to $3.20–$3.45 in 1962. By the end of 1963, quotations for the open-hearth, crucible, and primos grades containing 50 to 55 percent vanadium had dropped to $2.85–$3.05 per pound of contained vanadium, depending on the grade. At the end of March 1964, the price was down to $2.50 per pound of contained vanadium for all three grades, a price improving vanadium's competitive position with other alloying elements.

Vanadium metal of 90-percent purity has been quoted from $3.45 to $3.65 per pound for 100-pound lots since 1954. There are no published quotations for high-purity vanadium metal, but the price has been about $30 to $40 per pound since 1954.

RESEARCH

Research continues in government and industry on the extraction of vanadium from different materials and on application in various forms. Recently, interest has been generated in research on vanadium alloys for aerospace applications and on coatings for protection of such alloys against oxidation at high or moderately high temperatures. Current Bureau investigations include studies for an improved process for recovering vanadium from ferrophosphorus obtained as a byproduct, or waste product, of elemental phosphorus production from western phosphate rock; application of fused salt electrorefining techniques to preparation of high-purity ductile vanadium from commercially available vanadium materials; purification of vanadium with an electron-beam furnace; and basic research studies of the physical metallurgy of electrolytic vanadium and of vanadium-base chromium and tungsten alloys.

OUTLOOK

The vanadiferous uranium ores of the Colorado Plateau can no longer be expected to provide a surfeit of vanadium. However, considering other U.S. resources and the large deposits of South African vanadiferous magnetite, the supply will continue to be more than adequate. In addition, large Soviet supplies of vanadium may begin to appear on the world market by 1970.

Consumption of vanadium should continue to increase, possibly accelerating appreciably. New developments in the steel industry will account for the greater part of the increased demand. Greater use of the continuous casting

process will substitute vanadium for aluminum for killing deep-drawing steels such as are used in automobile bodies, shell cases, can tops, etc.; growing use of vanadium-bearing high-strength low-alloy steels by the construction industry will consume more vanadium; and the use of vanadium in line pipe and oil-drilling pipe will probably increase. Increased use of vanadium in various high-temperature and cryogenic applications can be anticipated, but it is doubtful that the quantity used will be of much significance compared with the aforementioned uses. Normal growth of the use of vanadium as a catalyst is expected. If a vanadium catalyst is found to be the answer to the automobile exhaust-smog problem, a large and continuing increase in demand would result. At present, however, there is no firm indication of such a development.

PROBLEMS

As the Colorado Plateau uranium ores of relatively high vanadium content become exhausted, the United States will have to turn increasingly toward one or more of the following sources: (1) vanadium ores of the Colorado Plateau with little or no recoverable uranium, (2) vanadium obtained as a byproduct or coproduct of Idaho phosphate or certain titaniferous magnetite mining operations, and (3) foreign sources of supply.

If the United States is to maintain self-sufficiency in vanadium, it will need to develop more economical methods of recovery so that this element can be obtained from the country's large low-grade deposits without dependence on coproducts.

The strong possibility of Soviet vanadium appearing on the market in substantial quantities can pose serious problems for present and prospective producers. The problem of continued ready availability of this vanadium becomes a concern for the consumer and those charged with government planning.

Cost is an important factor with regard to the position vanadium holds in competition with other alloying elements, particularly molybdenum and columbium.

Temperature and oxidation problems of vanadium and its alloys limit applications and present problems in working that challenge the research metallurgist.

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VERMICULITE

By Timothy C. May [1]

VERMICULITE expands into worm-like forms when suddenly subjected to heat. This curious bloating effect, known as exfoliation, is often so great that a plate of vermiculite, on heating, may swell up to 20 times its original thickness in a manner resembling the opening out of an accordion. The expanded vermiculite has many uses.

The first commercial production of vermiculite in the United States was in Colorado in 1915. There were five domestic producers in 1963, one of these accounting for nearly all of the output. The value of the exfoliated product was $14 million. The largest reserve is in Montana. In 1963, Montana and South Carolina were the largest producing States. Several foreign countries produce vermiculite, the largest foreign output coming from the Republic of South Africa.

Nineteen varieties of vermiculite have been identified and named, all hydrous magnesium aluminum silicates, mica-like minerals which can be exfoliated to as much as 20 times the original bulk on heating. Vermiculite is a secondary mineral, associated with basic host rocks and formed by hydrothermal alteration.

Mining is by open cut. The most advanced beneficiation is a wet method using hammermills, rodmills, classifiers, screens, table, and other standard beneficiation equipment and practices. Exfoliation is usually done in a vertical furnace, the ore falling by gravity against a series of baffles through a temperature zone ranking from 1,600° F to 2,000° F.

Uses are principally in construction as plaster and concrete aggregate and for loose fill insulation. Resources are large in the Western United States but are relatively small in the East. Substantial quantities of crude vermiculite are imported from the Republic of South Africa.

The outlook for vermiculite in the next few years is for a slight increase in production. Problems of the vermiculite industry include production of excessive fines and lack of market for these fines and byproduct biotite, health hazards and dust nuisance, high transportation costs, specification standards, and limited information on marketing and use.

BACKGROUND

In 1824, Thomas H. Webb, a mineralogist, described vermiculite from a deposit near Worcester, Mass. A variety of vermiculite first found in a serpentine quarry near West Chester, Pa., in 1851 by W. W. Jefferis was named jefferisite. Another variety was discovered in 1873 near the Culsagee River in Macon County, N.C., and named culsageeite. Since then other varieties have been found and named.

It was not until 1913 that deposits were discovered in Chaffee, Fremont, Custer, and Gunnison Counties, Colo. The first of these discoveries was by W. B. Thomas, in Chaffee County, 14 miles north of Salida, Colo. Only a small tonnage was produced from this source.

In 1915, the Denver Mining and Manufacturing Co. marketed vermiculite from a mine near Hecla, in Chaffee County. The product was sold under the trade name "Tung Ash" and classified at that time as a hydrated biotite mica (*4*).[2]

The most important domestic deposits were discovered in Montana by E. N. Alley, in 1916, while prospecting for vanadium. Continuous Montana production on a commercial scale began in 1921.

[1] Commodity specialist.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

Production from eastern deposits was first reported in 1929, from the Brinton quarry at West Chester, Pa., by the John Warren Watson Co. of Philadelphia, but the enterprise was not profitable. In 1933, deposits in North Carolina were opened near Ellijay in Macon County, but by 1959 all eastern vermiculite production came from South Carolina.

Important deposits in northeastern Transvaal, Republic of South Africa, became productive about 1938 (*9*).

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Five domestic operators mined vermiculite ore in 1963. They produced a total of 226,000 short tons of crude vermiculite valued at $3.6 million. The industry also has imported an average of 12,700 tons of crude annually during 1959–63.

In 1963 there were five domestic producers of vermiculite, American Vermiculite Co. and Patterson Vermiculite Co. operating in Laurens County, S.C.; W. R. Grace & Co., Zonolite Division, with several mines in South Carolina and one near Libby, Lincoln County, Mont.; Insuplast Inc., operating in Custer County, Colo.; and D.C. Howe in Platte County, Wyo. The W. R. Grace & Co., Zonolite Division, produces more than 90 percent of domestic crude vermiculite.

The ore mined is beneficiated and sized in the general vicinity of the mines and shipped to consuming centers in cities for exfoliation, bagging, and local distribution.

The largest domestic deposits are in Lincoln County, Mont., about 7 miles northeast of Libby (*1*). The Colorado deposits are probably next in potentiality, but as Montana now supplies the western and midwestern markets, and South Carolina, together with imports from the Republic of South Africa, serves the East, there is little current production from Colorado.

South Carolina has a number of relatively small developed deposits in Greenville, Spartanburg, and Laurens Counties, near Travelers Rest and Enoree. The Enoree area is currently the most active. North Carolina production came from deposits at Ellijay, Macon County, and from Swannanoa in Buncombe County.

By far the most important foreign vermiculite deposits discovered are in the Palabora region of northeastern Transvaal (*10*). The U.S.S.R. claims extensive deposits in the Ural Mountains, and production from this source has been confirmed.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Vermiculite is the name of the specific mineral and is also the commercial term applied to a group of micaceous minerals that expand greatly on rapid heating. The term also is used to denote the exfoliated product. In this report *crude vermiculite* means any of the vermiculite group minerals, beneficiated and sized, ready for the exfoliation furnace. They are all hydrous magnesium-aluminum silicates containing iron and other elements and have the characteristic micaceous lamellar structure and basal cleavage.

Nineteen varieties of vermiculite have been identified. Although there is some disagreement as to whether vermiculites constitute a distinct species, X-ray studies tend to confirm this as the defraction patterns of the vermiculites differ from the true micas or chlorite. Only the vermiculite and jefferisite varieties have been mined commercially.

Hardness ranges from 1.5 to 3.0 on Mohs' scale, and specific gravity of the crude material varies from about 2.30 to 2.80. In the crude state the color may be light brownish-yellow, dark yellowish-brown, or greenish, to almost black, often with a bronze cast. The streak is white, tenacity elastic to pliable, exfoliation temperature between 300° F and 1,500° F, and melting point between 2,425° F and 2,480° F. When heated in an open tube, the color changes to a gold, golden brown, or bronze, often with a metallic lustre. Heating in a reducing atmosphere gives crude vermiculite a silvery or almost white appearance.

Chemical composition is of little value in determining the expandability of vermiculite, and exfoliation tests provide the only satisfactory evaluation. The mineral can be identified in prospecting by heating with the flame of a candle or even a match.

When used for loose fill insulation, exfoliated vermiculite is sized to minus 3- plus 14-mesh and weighs 5 to 6 pounds per cubic foot. For concrete aggregate, a minus 5- plus 20-mesh exfoliated vermiculite is usually recommended, replacing sand, gravel, or crushed stone. Other commercial screen size ranges are minus 8- plus 65-, minus 10- plus 65-, and minus 20- plus 100-mesh (Tyler standard screen sizes) (*8*). Vermiculite concrete weighs from 16 to 50 pounds per cubic foot and has a compressive strength of 50 to 500 pounds per square inch compared with 150 pounds per cubic foot for concrete made with sand and gravel aggregate having compressive strength of 1,300 to 3,000 pounds per square inch. The thermal conductivity (k-factor) is

0.60 to 1.9 Btu per square foot per inch thickness, per hour, per degree F, depending principally on the mix ratio, which governs the unit weight of the concrete. The proportions of the mix usually are 1 cubic foot portland cement (1 bag), 3 cubic feet of stabilized vermiculite concrete aggregate (¾ bag), and 2 cubic feet of sand. The lighter the concrete, the more sealed air spaces are present, with a corresponding lowering of the k-factor and greater efficiency as insulation. Air-entraining agents are used with vermiculite concrete and are introduced as a dry additive in the proportion of about 5 ounces per 4-cubic foot bag of exfoliated vermiculite.

The finer exfoliated sizes, down to 100-mesh, are used in vermiculite plaster for walls and ceilings to insulate against heat and sound and as fireproofing around beams, girders, and columns. Vermiculite base-coat plaster is made by adding 6 bags of vermiculite aggregate to 9 bags of gypsum plaster. The finish coat is composed of 1 bag vermiculite aggregate, 2 bags unfibered gypsum plaster, and 16 gallons of water. A 4-hour fire rating was issued in 1939 on a ⅞-inch thickness of vermiculite plaster on metal lath to fireproof a steel floor assembly. Since then many fire ratings for various types of construction and fireproofing have been developed. Vermiculite has contributed materially to the improvement of modern lightweight building construction (*11*).

TECHNOLOGY

Geology

Vermiculite is associated with basic rocks such as pyroxenite, peridotite, dunite, and serpentine, often in the vicinity of pegmatite dikes or other acid intrusives. Associated minerals frequently are quartz, feldspar, apatite, kyanite, corundum, biotite, chlorite, phlogopite, asbestos, talc, and clay minerals. A few occurrences have been reported unassociated with basic rocks, but in such instances the deposits were small, and the vermiculite did not exfoliate satisfactorily. Extensive "horses" of unaltered biotite are found in the South Carolina vermiculite deposits.

The vermiculites are believed to be formed by hydrothermal action on the ultrabasic igneous host rocks or by the alteration of biotite, phlogopite, chlorite, or other minerals of similar chemical composition. Weathering may play an important part in the alteration cycle.

The following chemical analyses are typical of the three major vermiculite deposits (*8*):

TABLE 1.—*Analyses of unexfoliated vermiculite*

[Percent]

	Source of material		
	Libby, Mont.	Enoree, S.C.	Palabora, Transvaal, Republic of South Africa
SiO_2	38.64	38.66	39.37
MgO	22.68	20.04	23.37
Al_2O_3	14.94	17.36	12.08
Fe_2O_3	9.29	8.45	5.45
FeO			1.17
K_2O	7.84	5.24	
CaO	1.23	.75	1.46
Cr_2O_3	.29	.50	
Mn_3O_4	.11	.12	
P_2O_5	Trace	Trace	
S	Trace	Trace	
Cl	.28	.52	
H_2O	5.29	8.71	11.38

Mining

Although some underground mining of vermiculite has been done, all 1963 production was from open-cut mines. The usual practice is to strip the overburden with hydraulic scrapers and dig the vermiculite ore from the face with power shovels loading into trucks. Benches are established if the ore has a vertical thickness of over 25 feet. Although some blasting of dikes and barren rock may be needed, the vermiculite ore is soft and easily handled by the shovel or dragline excavator without blasting. The ore carries from 25 to 95 percent vermiculite, the gangue consisting principally of clay and boulders from the dikes and country rock with which the vermiculite is associated.

Beneficiation

Until recently domestic vermiculite ore was beneficiated by dry methods using screens, direct-fired dryers, pneumatic tables, and air separators. Partly because of the dust hazard, wet methods are now used in the mills of the largest mines. Hammer mills, rod mills, rake classifiers, screens, wet cyclones, and tables are used to separate the vermiculite flakes, remove adhering clay and other impurities by scrubbing and washing, and to concentrate and size the vermiculite. Drying is done by centrifuge and direct-fired rotary drier.

Exfoliation has been done in furnaces of only slight inclination and also those of vertical design. The latter type now is used predominantly in commercial expanding operations. The inner walls are of fire brick with an outer wall of insulating brick. Baffles in the heating chamber impede the fall of the crude ore which is fed in near the top of the furnace. Gas or fuel oil is used for heating,

and the charge is usually exposed to a temperature of between 1,600° F and 2,000° F for from 4 to 8 seconds.

Exfoliation is caused by the pressure of steam generated when the water of composition is heated to a high enough temperature. This forces the laminae apart in a direction at right angles to the cleavage planes, in an accordion-like form. This is also accompanied by considerable warping of the individual laminae. Innumerable air spaces are thus developed throughout the heated vermiculite, imparting to the mass the great bulk and insulating qualities which give it commercial value. The ultimate crystalline sheet into which vermiculite can be split measures only 10 angstrom units (25 such sheets piled on top of one another would measure about 1 millionth of an inch) (*5*). This provides a great expansion potential as the water of crystallization is turned to steam between the lamellae.

Too much time in the hot zone of the furnace removes additional combined water after optimum exfoliation has been achieved. This has a deleterious effect on the vermiculite, reduces toughness and pliability, and causes brittleness.

An airlift separates the exfoliated vermiculite from rock and other unexpanded waste material, and an air current then carries the exfoliated material to the bagging department. It also cools the vermiculite so packaging can be done without scorching the bags.

The friable nature of vermiculite is the cause of considerable dust in the plant during exfoliation, sizing, and bagging.

The usual exfoliating furnace has an hourly capacity of over seventy 4-cubic-foot bags, the standard packing unit. Although fines are necessarily produced, little minus 100-mesh vermiculite is marketable. The matter of fines is a serious major problem with all producers.

USES

It is estimated that over 50 percent of all exfoliated vermiculite is used in building and construction, and much of this is used as concrete aggregate. Lightweight-plaster aggregate and loose-fill insulation are also important uses. In plaster, vermiculite improves insulation and fire resistance and reduces fuel costs. The innumerable minute air cells within the exfoliated vermiculite retard the passage of heat and sound through the mass. Standard mixtures for vermiculite plaster and concretes with approximate corresponding coverages, are available from The Vermiculite Institute (*11*).

One ton of loose exfoliated vermiculite will cover about 1,120 square feet of area to a depth of 3 inches and provide excellent thermal insulation.

Vermiculite is used for packing refrigerators, cold storage rooms, incubators, fireless cookers, thermal jugs, ovens, safes, and water heaters. As a refractory, vermiculite with a suitable binder and applied as a plastic mass can withstand furnace temperatures to 1,800° F.

Other uses include horticulture, carriers for herbicides, insecticides, fungicides and fumigants, hatchery litter, refractory fire brick, and beds for transporting hot steel ingots.

As a filler, vermiculite has applications in plastics, rubber, paints, printing inks, and oil well cements. For other uses, it is bonded with many binders, including dextrin, casein glue, wood pulp, clays, plaster of paris, portland cement, synthetic resins, and waterglass. In combination with asphalt, vermiculite is used in roofing and flooring compositions.

Exfoliated vermiculite is used as a soil additive for rooting cuttings and tubers in hotbeds, for sprouting seedlings, and as a general soil conditioner mainly to lighten clay soil or to improve the moisture-retention qualities of sandy soils.

The coarsest exfoliated vermiculite, around ½-inch particle size, is used in poultry hatcheries as a litter. The medium-size range is marketed as a loose fill insulation between the studding and beams of walls, floors, and roofs, for lightweight aggregate, plaster and concrete, and as a soil conditioner. Some applications for sizes below 100-mesh are:

- Grease lubricants
- Filler in plastics
- Tire and rubber goods
- Wallpaper printing
- Outdoor advertising paints
- Anti-caking agent in fertilizers
- Increasing viscosity of oil
- Fireproof containers for photographic films
- Extender for gold and bronze printing inks and for paint
- Carriers for agricultural chemicals, insecticides, herbicides, and fungicides

A data book has been published listing uses for vermiculite, including information on absorption, resiliency, thermal expansion, and other characteristics in filler, lubricant, catalyst, dielectric, and insulator applications (*12*).

ALTERNATE MATERIALS

Vermiculite encounters several long-established competitive commodities in all its fields of use. As plaster aggregate, it must compete with silica sand, expanded perlite, and pumice. Competitive lightweight concrete aggregates

are expanded clay, slate, shale, and slag, expanded perlite, cinders, pumice, sawdust, organic fibers, foamed glass, and calcined diatomaceous earth. Air-entraining agents which lighten ordinary concrete also can be considered a lightweight aggregate substitute. Mineral wool, expanded perlite, pumice, diatomaceous earth, cork, and sawdust compete with vermiculite as loose fill insulation. In oil well cementing, perlite and clays, including bentonite, are competitive materials.

There are many fillers and extenders with which vermiculite must share the market. Some of these are perlite, feldspar, gypsum, mica, pumice, talc, limestone, kaolin, silica sand, diatomite, barite, and synthetic calcium silicates.

As a soil conditioner, vermiculite competes with perlite, peat, and synthetic soil conditioners.

RESERVES

Substantial vermiculite resources occur in Colorado, North and South Carolina, and Montana, principally in the latter State, in Lincoln County and in the southern extension of the Madison and Gallatin Ranges north of Yellowstone National Park, in the Rocky Boy Indian Reservation in Hill County, and also about 12 miles east of Hamilton in Ravalli County. Other States have potentially important but unexplored resources. Vermiculite deposits have been reported in Arkansas, California, Georgia, Massachusetts, Nevada, Pennsylvania, Texas, and Wyoming.

The largest known foreign resources are in Africa, particularly in Transvaal Province, the Republic of South Africa. Other African deposits are in Tanganyika, Kenya, Uganda, Southern Rhodesia, United Arab Republic (Egypt), and Morocco (*10*).

Vermiculite also occurs in southeastern Western Australia, at Bulong and Kalgoorlie. A Canadian deposit near Stanleyville, Lanark County, Ontario, is said to have commercial possibilities (*3*). Japan has vermiculite in the Kadzua Peninsula and in the Hajikano area, Province of Yamanashi-ken. Other foreign sources are Argentina, India, Brazil, Chile, and Mexico.

SOURCES OF STATISTICAL INFORMATION

The Bureau of Mines, U.S. Department of the Interior, canvasses producers of crude and exfoliated vermiculite annually, and publishes resultant data in Minerals Yearbook. A Census of Mineral Industries intermittently presents vermiculite industry statistics for single years.

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PRODUCTION, CONSUMPTION, AND TRADE

The quantity of exfoliated vermiculite sold or used in 1963 was 24 percent less than the quantity of crude vermiculite reported produced. This difference was partially due to changes in stocks and loss of fines formed in the exfoliation processes and to the rejection of waste rock and unexfoliated vermiculite during the operation.

Although statistics on producers' or consumers' stocks are not collected by the Bureau of Mines or The Vermiculite Institute, supplies of currently unmarketable fines are known to be substantial.

Colorado was the first State to record commercial production of crude vermiculite in 1915, but Montana has been the leading producer since 1922.

In 1963 the first six States, in order of production of exfoliated vermiculite were California, Illinois, Texas, New Jersey, Minnesota, and Florida.

Vermiculite data are combined with a variety of other nonmetallic minerals in government foreign trade statistics. About 85 percent of the vermiculite exfoliated in Canada came from the United States in 1963. Canada imported almost Can$497,000 of crude vermiculite from the United States and Can$77,000 from the Republic of South Africa in 1963.

The Republic of South Africa ships substantial quantities of crude from several operations to world markets, including the United States. Exports of crude to the United States, in short tons, are reported from the Republic of South Africa for the years 1959 through 1963 as follows: 1959—11,827; 1960—12,396; 1961—12,913; 1962—12,098; 1963—14,337.

Crude vermiculite may be imported duty free under paragraph 1719 of the Tariff Act of 1930. Exfoliated vermiculite carries a duty of 15 percent ad valorem but the bulk of exfoliated vermiculite ordinarily precludes its importation into the United States.

TABLE 2.—*Crude and exfoliated vermiculite sold or used by producers in the United States*

	1959	1960	1961	1962	1963
Crude vermiculite:					
Thousand short tons	207	199	206	205	226
Value, thousands	$3,082	$3,108	$3,350	$3,293	$3,572
Average value per ton	$14.89	$15.62	$16.26	$16.06	$15.81
Exfoliated vermiculite:					
Thousand short tons	153	151	151	152	172
Value, thousands	$9,591	$10,305	$10,787	$11,152	$13,877
Average value per ton	$62.69	$68.25	$71.44	$73.37	$80.68

PRICES

The average annual value of domestic crude vermiculite has been more nearly constant than most other industrial mineral prices. The average for 1949–58 was $12.66 per ton f.o.b. producer's plant. Values of both crude and exfoliated vermiculite for 1959–63 are shown in table 2.

TAXES

Federal tax statutes permit a 15-percent depletion allowance on the value of domestic and foreign crude vermiculite.

TRANSPORTATION

Montana supplies crude vermiculite to exfoliators from the Midwest to the Pacific Coast areas and the Pacific export markets; the South Carolina output is distributed from the Midwest to the eastern seaboard and Atlantic export markets. Imports from Africa compete with some eastern domestic sources for eastern coastal markets. Transportation cost is an important competitive feature in this industry.

Exfoliated vermiculite has great bulk in proportion to its weight. Therefore, the washed and sized crude vermiculite is shipped from the mines to exfoliation plants in the consuming areas.

Packaged exfoliated vermiculite is sold in 4-cubic foot paper bags which range in weight from 24 pounds per bag for very coarse material to 35 pounds for very fine product. The average is about 7½ pounds per cubic foot, dry basis. This compares with an average for expanded perlite of from 3 to 6 pounds per cubic foot, 9 pounds for diatomite, and 100 pounds for ordinary sand. The weight of pumice per cubic foot ranges from 15 pounds to almost that of obsidian.

RESEARCH

The Vermiculite Institute promotes the welfare of the vermiculite industry, publicizes its advantages, advocates its increased use, works for approval of its applications in city building codes, and develops fire ratings. In pursuit of these objectives, research has been conducted by this Institute, assisted by the producers. Many construction designs embodying the use of vermiculite have been published by the Institute (*11*).

Studies and comparisons were made by the Housing and Home Finance Agency of concretes using exfoliated vermiculite aggregates, other lightweight materials, and ordinary dense sand and gravel (*6*).

Studies by the Bureau of Mines have covered a number of aspects including influence of temperature, heating time, moisture and flake size on exfoliation, percentage of voids, hydraulic, air and screen classification, tabling, flotation, and comparative insulating values. Details of the work accomplished are reported in three publications (*2*, *7*, *13*).

OUTLOOK

The growth in the consumption of vermiculite will be influenced largely by the volume of future residence and public building activity. Over the short term period (5 years) production of crude vermiculite is expected to reach 300,000 tons by 1970, or an increase of 5 percent annually during the 1965–70 period.

The trend in construction design is toward the greater use of lightweight aggregate concrete and consumption of vermiculite is expected to increase from that source as well as the use of vermiculite as a masonry fill. Vermiculite for accoustical and fireproofing purposes, pipe covering, and horticulture is expected to maintain the gradual increase in usage.

The large resources of vermiculite presently known indicate that the supply will be adequate to meet foreseeable requirements.

PROBLEMS

Freight rates for shipping the ore from the mine to exfoliating plants are significant in the cost of the expanded material. High transportation costs from present major commercial sources of crude vermiculite to the major market areas are a serious commodity problem.

Inadequate information on the consumption of exfoliated vermiculite has impeded understanding of the demand picture.

Many of the architectural design manuals of the military departments have been revised to permit the use of vermiculite masonry fill. There are some building codes, however, that restrict the full utilization of vermiculite.

Since there are differences in the inherent expandability of different vermiculites, the volume to which a given size will expand is important to the purchaser of vermiculite con-

centrates. Studies are needed of the physical, chemical, and processing characteristics of vermiculites from different sources for determining their commercial potentialities.

Another problem of the industry is to find an outlet for fines produced in processing and for the residual biotite occurring in some vermiculite deposits.

Dust produced in exfoliating plants cause health hazards. Installation of dust collection systems in many plants has relieved this problem to a great extent.

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WATER

By William H. Kerns [1]

WATER is recognized as one of the most important natural resources of the world. An adequate supply of this precious mineral, for man's ever-increasing requirements for personal use, for agricultural, mining, and manufacturing industries is essential to the continued welfare and advancement of modern civilization.

This chapter presents the salient facts and problems of water supply and demand with special emphasis on water use and problems in the mineral industry. If the economy of the United States is to continue to grow and prosper, there must be adequate supplies of water available.

The nature, the immediacy, and the gravity of the water resources problems faced by the United States vary greatly from region to region; however, all parts of the country either have or will have water problems. The well-watered Eastern and Southern States are beginning to share a concern about water that has been felt in the arid West since its settlement. As industrial development and urbanization expand in the East, it is becoming more apparent each year that lack of water may deter growth unless action is taken to assure a continued supply.

The withdrawal of water, now about 300 billion gallons daily (bgd), is expected to double or be 51 percent of the streamflow by 1980 and triple or be 81 percent of the streamflow by the year 2000, if present trends are continued. However, most of the water withdrawn is returned to streams and can be reused many times, provided steps are taken to maintain its quality. Consumptive uses and depletions are expected to be 17 percent of the available streamflow in 1980 and 23 percent in the year 2000.

From this, it appears that our overall water resources are abundant and sufficient for many years to come if we concentrate our efforts in certain areas. Five of the more important categories of effort needed in meeting future prospective water demands include (1) maintaining water quality through pollution abatement in order to increase reuse of water; (2) regulating streamflow by means of constructing surface reservoirs and watershed management; (3) making better use of underground storage; (4) increasing the efficiency with which water is used through improved sewage treatment methods, recirculation, increased irrigation efficiency, substitution of air cooling for water cooling, and elimination of wasteful practices; and (5) increasing the natural water yield by desalting, weather modification, and other artificial means.

Of the six principal water-using manufacturing industries that accounted for 81 percent of the total water requirements for manufacturing in the United States in 1959, four—iron and steel, chemical, aluminum, and copper, which represented 72 percent of the total manufacturing—are a part of the mineral industry. The projected total water requirement for these six manufacturing industries for 1980 is 26,500 billion gallons yearly (bgy), nearly three times that in 1959, and is expected to be 61,600 bgy, more than six times the 1959 requirement, by 2000.

For selected nonmanufacturing segments of the mineral industry in the United States in 1962, a total of 1,030 bgy of new water was withdrawn and 2,563 bgy was recirculated, making a total of 3,593 bgy required or used. Of the total new water withdrawn, 774 bgy or 75 percent was discharged for reuse and 257 bgy or 25 percent was consumed by evaporation or by shipment in the product. By 1980 demand for new-water intake for these selected nonmanufacturing segments of the mineral industry is expected to double to more than 2,000 bgy and by the year 2000 to quadruple to more than 4,000 bgy.

The pressing problems concerning water resources in the mineral industry follow closely the national water problems. An adequate quantity and quality of water must be provided or developed at the place and time needed to mine and process minerals to meet the present and future ever-increasing needs for them. In

[1] Commodity specialist.

some areas ways must be provided to handle too abundant water that floods mines or flows from mines or mined-out areas. Ways must be found to reuse or recirculate more water in order to conserve water and to replace some of the new-water intake. Disposal of mining and metallurgical wastes to abate stream pollution is a major problem. Statistical data must be collected through detailed studies in water-short mineral-producing areas, and national canvasses of water use in the mineral industry must be conducted as the basis for understanding and projecting future requirements for this essential industry.

BACKGROUND

Water is mankind's single most valuable natural resource. Science tells us that the earliest forms of life began in the vast oceans of the primeval earth. The human body is over 70 percent water. Without water, life as we know it would perish from the earth. Water has been the key to man's advancement since the beginning of recorded history. The earliest civilizations were established where water supplies were available. Recorded history began in the valleys of the Tigris and Euphrates and along the Nile. According to many historians, the decline and disappearance from the face of the earth of ancient civilizations in many of the arid or semiarid regions began with man's failure to properly use his available water resources.

Water is assuming an ever-increasing importance as civilization's needs for water and water related products and services grow. Areas of this globe that will thrive, or even survive, will be determined by the availability of water and its wise use to serve man. The development of water resources is of strategic importance in nearly every country possessing unused natural resources and having ambitions to secure a higher standard of living for its people.

MAGNITUDE AND GEOGRAPHIC DISTRIBUTION OF WATER SUPPLY

Water is the most abundant substance on our planet. The earth is sometimes called the water planet because it is the only member of our solar system known to contain large quantities of water on its surface. Nearly all of our planet's water is salty, which is satisfactory for the creatures that live in the sea; however, land plants and animals must have fresh water. They can live only because the sun continually distills pure water from the oceans, and this water is carried in the air until it condenses and drops on the land. The flux of water from the ocean into the air, onto the land, and back to the sea is called the hydrologic cycle or water cycle.

The water that falls as rain on the United States averages about 5 billion acre-feet of water per year, sufficient to cover the area to a depth of 2½ feet if it were uniformly distributed. Many parts of this country either have or will have water supply problems. However, with its abundant supply of good water and its advanced technology and skills, the United States need never suffer for lack of water.

The water resource of the United States that is derived from precipitation varies geographically as well as seasonably and yearly. However, it is a perennial supply, which on a long-term basis approaches a constant for the Nation, averaging about 30 inches a year. In many Southern and Eastern States the annual precipitation is considerably above the national average, while in most of the West and Southwest it is below average. For example, average precipitation at Greenland Ranch, Death Valley, Calif., is 2 inches per year compared with more than 150 inches at Wynoochee, near Aberdeen, Wash. At Little Port Walter, Alaska, total precipitation was 269 inches in 1943, while at Mt. Waialeale, Hawaii, the average annual precipitation is reported to be 471.68 inches, the heaviest recorded rainfall in the world.

Of the national 30-inch-average annual precipitation, 21 inches or 70 percent returns to the atmosphere by evaporation or transpiration. This water is not all wasted because a part of it supports cultivated crops, forests, and native grass. The remaining 9 inches, draining from land surface and ground-water seepage, is the manageable supply. From this runoff, 3 inches is withdrawn for all uses, of which 1 inch returns to the atmosphere and 2 inches is returned to the streams, lakes, oceans, or ground. Of the 3 inches withdrawn for use, 80 percent is from lakes and streams and the remaining 20 percent is from wells.

The manageable supply, commonly called the water supply potential, as measured by runoff, is 1,200 bgd. Of this total, 269 bgd is withdrawn for all uses exclusive of water used to develop waterpower. Of this water withdrawn, 62 bgd is consumed. Total dependable supply in 1980 is estimated at 515 bgd and in some water-use regions such as South Pacific (California) and Western Gulf (most of Texas

and New Mexico) the estimated dependable supply for 1980 is less than the withdrawals in 1960. Water-use regions in the United States are shown in figure 1 and water supply potential and use, runoff, withdrawals, and water consumed in 1960, and estimated dependable supply in 1980, are shown by region in table 1 (*20*).[2]

In the 1961 final report (*31*) of the Senate Select Committee on National Water Resources, U.S. Congress, the contiguous United States was divided into 22 water resources regions slightly different from the Federal Geological Survey regions shown on figure 1. According to this committee, substantial areas of water shortages already exist in many of the river basins in the western one-half of the United States. By 1980 or earlier, full development of all of the available water resources in 5 of the 22 regions will be required if the economic development is achieved that is necessary to support the Nation's ever-increasing population. The five regions are (1) South Pacific (lower one-third of California), (2) Colorado River (similar to that shown for Colorado region on fig. 1), (3) Great Basin (as shown on fig. 1), (4) Upper Rio Grande-Pecos River (western one-half of Western Gulf region on fig. 1), and (5) Upper Missouri River (as shown on fig. 1). By the year 2000, three more regions will be added to the list of those in which full development of available water resources will be required if the projected demands are to be met. These regions include (1) Upper Arkansas-Red Riv-

[2] Italicized numbers in parentheses refer to items in the references at the end of this chapter.

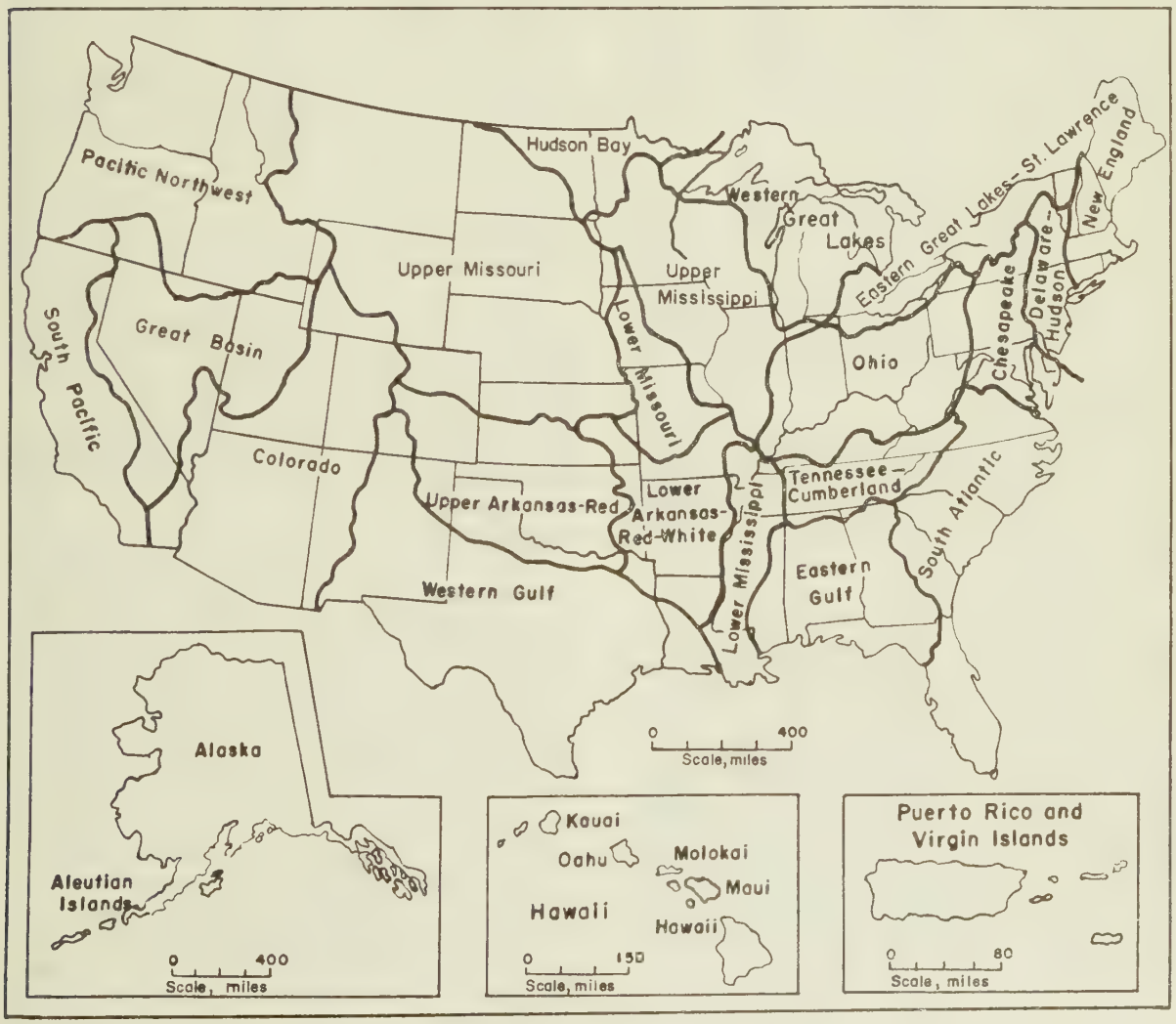

FIGURE 1.—Water-use Regions (*20*).

(Federal Geological Survey)

TABLE 1.—*U.S. water supply potential and use (20)*

Region	Area (thousand square miles)	Runoff		Estimated dependable supply, 1980 (billion gallons per day)	Withdrawals, 1960 (billion gallons per day)	Water consumed, 1960 (billion gallons per day)
		Inches per year, average	Billion gallons per day			
New England	59	24	67	22	6.4	0.3
Delaware-Hudson	31	21	32	24	20	.8
Chesapeake	57	19	51	12	7.1	.3
South Atlantic	170	14	110	75	13	1.5
Eastern Gulf	109	19	99		5.9	.5
Tennessee-Cumberland	59	21	59	22	7.5	.4
Ohio	145	16	110	40	24	.8
Eastern Great Lakes-St. Lawrence	47	18	40	30	13	.4
Western Great Lakes	81	11	42	36	16	.5
Hudson Bay	60	1.6	4.6		.2	.1
Upper Mississippi	182	7.2	62	31	11	.6
Upper Missouri	458	1.0	24	33	20	7.4
Lower Missouri	62	7.8	23		1.6	.2
Lower Mississippi	64	16	49	25	5.3	1.3
Upper Arkansas-Red	153	1.6	11	20	5.5	3.2
Lower Arkansas-Red-White	117	14	79		4.9	.9
Western Gulf	341	3.2	52	20	22	9.2
Colorado	258	1.1	13	15	14	7.1
Great Basin	200	1.1	10	9	7	3.3
South Pacific	112	12	64	28	33	13.0
Pacific Northwest	257	13	159	70	29	8.3
Total	3 022	----------	1,200	515	266.4	60.1
Hawaii	6	----------	----------	----------	1.6	.4
Alaska	586	----------	----------	----------	.2	----------
Puerto Rico	3	----------	----------	----------	1.2	.3
Grand total	3,617	----------	----------	----------	269.4	61.8

ers (as shown on fig. 1), (2) Western Great Lakes (as shown on fig. 1), and (3) Western Gulf (eastern one-half of Western Gulf region as shown on fig. 1).

The Bureau of Mines has a continuing program of cooperation with other Government agencies in the preparation of comprehensive water development plans for all major river basins of the United States along the lines suggested by the Senate Select Committee on National Water Resources.

Water usage data from the Bureau of Mines canvass of selected nonmanufacturing segments of the mineral industry, by States, in 1962 are shown in table 2. Including the metals, nonmetals, coal, and natural gas processing components and excluding the oil well drilling and secondary-recovery operations, the major water-using States were Texas, Florida, Louisiana, California, and Minnesota, which together accounted for 55 percent of the total water usage by the major components covered. For this same grouping of mineral industries, Texas, Tennessee, Utah, Arizona, and Florida were the largest water-consuming States, which together consumed 57 percent of the total.

A comprehensive State-by-State report on the Nation's water resources was published (*22*) that both reassures and cautions all who have an interest in the water situation. It shows that, despite the availability of water reserves underground, the intensity of surface and ground water development in this country has led to local shortages and acute water problems, such as permanent lowering of the water table in certain areas or the encroachment of salt water in coastal streams and wells.

Reports on the mineral and water resources of seven States—Alaska, Colorado, Nevada, Idaho, Montana, South Dakota, and Utah—have been prepared for the Senate Committee on Interior and Insular Affairs and published as committee prints. Detailed data are given for the water situation in each of these States: surface and ground water supply, utilization and storage, waterpower, and selected references. Reports for other States are under preparation.

In the East, where water is relatively plentiful except for some localized areas, there are mounting pollution problems in otherwise usable water supplies. In the West, industry—and with it, population—is moving into precisely those areas where the available water supply already is limited. To ease the water situation in such areas several transmountain water-diversion plans have been proposed.

TABLE 2.—*Water usage in selected segments of the mineral industry, by States, 1962* [1]

[Million gallons per year]

State	Total metals, nonmetals, coal, and natural gas processing industries					Petroleum well-drilling and secondary-recovery operations (total water usage)
	New water	Water recirculated	Total water usage	Water discharged	Water consumed	
Alabama	6,638	9,851	16,489	5,608	1,030	11
Alaska	18,344	3,359	21,703	17,856	488	52
Arizona	27,304	50,203	77,507	13,811	13,493	5
Arkansas	9,538	15,056	24,594	8,053	1,485	1,585
California	68,929	141,422	210,351	63,853	5,076	20,549
Colorado	10,155	29,098	39,253	7,827	2,328	3,900
Connecticut	2,274	711	2,985	2,105	169	----------
Delaware	112	41	153	105	7	----------
Florida	75,407	179,131	254,538	64,919	10,488	2
Georgia	14,760	1,882	16,642	13,918	842	----------
Hawaii	328	----------	328	327	1	----------
Idaho	10,034	1,856	11,890	9,700	334	----------
Illinois	14,765	44,131	58,896	14,086	679	17,753
Indiana	8,920	17,805	26,725	8,489	431	1,055
Iowa	2,011	3,937	5,948	1,966	45	----------
Kansas	14,058	31,837	45,895	13,202	856	14,211
Kentucky	9,612	31,862	41,474	8,866	746	2,547
Louisiana	74,490	139,144	213,634	69,099	5,391	5,566
Maine	206	14	220	195	11	----------
Maryland	5,195	2,313	7,508	4,804	391	1
Massachusetts	2,614	1,778	4,392	2,442	172	----------
Michigan	47,296	40,841	88,137	46,094	1,202	286
Minnesota	102,314	99,224	201,538	97,938	4,376	----------
Mississippi	7,076	6,758	13,834	6,746	330	804
Missouri	15,776	10,167	25,943	15,011	765	1
Montana	9,673	8,592	18,265	8,891	782	612
Nebraska	1,839	6,499	8,338	1,581	258	2,118
Nevada	8,577	3,817	12,394	5,211	3,366	1
New Hampshire	643	429	1,072	609	34	----------
New Jersey	12,890	9,296	22,186	12,451	439	----------
New Mexico	13,083	170,456	183,539	5,306	7,777	2,737
New York	20,172	11,376	31,548	18,064	2,108	1,462
North Carolina	7,898	3,775	11,673	7,224	674	----------
North Dakota	2,189	5,046	7,235	2,108	81	1,202
Ohio	32,701	19,808	52,509	28,782	3,919	412
Oklahoma	8,603	181,631	190,234	6,213	2,390	47,501
Oregon	2,909	36	2,945	2,743	166	2
Pennsylvania	41,972	50,996	92,968	38,318	3,654	6,940
Rhode Island	506	86	592	461	45	----------
South Carolina	3,887	1,956	5,843	3,812	75	----------
South Dakota	3,351	1,245	4,596	2,705	646	1
Tennessee	57,304	97,168	154,472	37,819	19,485	49
Texas	66,070	921,199	987,269	38,472	27,598	54,965
Utah	23,356	40,211	63,567	10,384	12,972	608
Vermont	582	148	730	525	57	----------
Virginia	6,968	11,142	18,110	6,143	825	1
Washington	7,896	1,174	9,070	7,484	412	3
West Virginia	20,464	61,367	81,831	15,716	4,748	130
Wisconsin	1,870	1,168	3,038	1,818	52	----------
Wyoming	5,299	18,145	23,444	3,011	2,288	8,578
Total	908,858	2,489,187	3,398,045	762,871	145,987	195,650

[1] Data may be slightly different from those shown in vols. I and III of Minerals Yearbook 1963 because of rounding and minor revisions.

Suggestions by the U.S. Department of the Interior include the Southwest Pacific Plan and the Central Arizona Project, which call for diversion of water from northern to southern California, and probably eventually into Arizona. Other proposals by the Department include the San Juan-Chama Project (Colorado to Rio Grande basins) and Frying Pan-Arkansas Project (Colorado to Arkansas basins).

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Water is such a common substance that many of its unusual properties are overlooked. It is one of the two mineral substances that are liquid at ordinary temperatures, the other being mercury. Water is denser as a liquid than as a solid. Without this property lakes and ponds would freeze from the bottom up and life, as we know it, could not have developed.

Water's high specific heat and high latent heat of vaporization make it an excellent substance for transferring heat energy. The kinetic energy of a moving column of water is utilized in spinning turbines for power generation and in hydraulic placer mining. The property of water which enables it to dissolve, entrain, and suspend many substances makes it a convenient tool of industry for transporting, mixing, grinding, separating, and cleaning the many material substances required by modern society.

The fact that water dissolves or entrains many sustances strongly affects its physical and chemical properties. Suspended solids are generally more easily removed than dissolved solids, many of which adversely affect the use of the water. Some of these contaminants cause corrosion and others, such as calcium and magnesium, cause scaling and interfere with the cleansing action of soap in water by precipitating the soap. Water containing appreciable quantities of calcium and magnesium are classed as hard waters.

For drinking water the Federal Public Health Service recommends that the total dissolved solids should not exceed 500 parts per million (ppm), although 1,000 ppm is permitted on interstate carriers when water of better quality is not available. The mineral content of good irrigation water should not exceed 1,400 ppm, with special restrictions on the sodium ion. Radioactivity limits for drinking water were established in microcuries per liter as follows: 3 for radium 226; 10 for strontium 90; and 1,000 for gross beta activity (*33*).

Water having more than about 1,000 ppm of dissolved solids is said to be slightly saline; between 3,000 and 10,000 ppm it is moderately saline; with more than 10,000 ppm it is very saline; and with 35,000 ppm and over it is characterized as brine. Ocean water usually ranges from 33,000 to 35,000 ppm. In most saline waters the sodium and chloride ions predominate; however, significant quantities of Ca, Mg, K, Fe, Mn, SiO_2, HCO_3^-, and SO_4^{--} are also present.

With the rapid growth of nuclear science the term "heavy water" has become common. Heavy water, or deuterium oxide (D_2O), consists of deuterium, a heavy isotope of hydrogen, combined with oxygen in the usual ratio. Although similar to ordinary water, heavy water differs in several of its properties, being slightly more dense and viscous.

Definitions of the terms used in the Bureau of Mines canvass of the selected nonmanufacturing segments of mineral industries in 1962 are as follows:

New-water intake.—Water introduced into the operation for the first time regardless of quality or source.

Recirculated or transferred water.—Water that is returned or transferred for reuse for the purpose of reducing new-water demand.

Water use or usage.—Summation of new water and recirculated or transferred water.

Recycled solvent.—Solutions such as leaching and cyanide solutions, reused for metallurgical processing.

Water discharged.—Water returned to streams, lakes, or to the ground.

Water consumed.—Water evaporated or incorporated and shipped in product.

TECHNOLOGY

An exhaustive study of U.S. water problems covering virtually every aspect of the technology of water—its sources, location, conservation, uses, management, and economics—was made by Resources for the Future, Inc. (*1*). The study treats primarily the proven technology which has influenced water development in the past or which still is effective in shaping its course; however, it also treats the emerging technology of today. It will serve as an excellent factual background or reference for relating technology to water development and water policy decisions.

Abatement of the pollution of our water resources is a pressing technologic problem. Pollution is a threat to public health and to the economic and social welfare of our people. A National Conference on Water Pollution (*34*), called by the President in 1960, assessed the problem of water pollution, determined its effects upon our national welfare, and set realistic goals for its control.

A study of subsurface waste disposal of industrial wastes in the United States revealed that in an area of eight States a wide variety of

industrial wastes is being injected into formations ranging in age from Precambrian to Recent (*10*). In this area more than 30 wells ranging in depth from 300 to 12,000 feet are used for waste disposal into subsurface formations which include unconsolidated sand, sandstone, vugular limestone, and fractured gneiss.

Most uses of water have rather specific quality requirements, and for this reason water treatment is usually necessary. Treatment of water for municipal uses generally consists of settling and filtration to remove suspended matter, chlorination to kill residual microorganisms, and aeration for odor control. In some States water treatment includes the addition of small quantities of fluorine-containing compounds. Water is also treated to reduce its hardness. This treatment removes a high proportion of the calcium and magnesium ions that increase soap and detergent requirements and cause scaling in boilers.

Treatment of waterborne wastes is becoming increasingly complex, not only because of increasing quantities of waste but also because, in the production of many new chemical and medicinal substances, new types of industrial and mineral wastes are being produced. Increasing use of mineral detergents in place of ordinary soap causes difficulties with standard water- and sewage-treatment processes.

New-water intake (1,029,800 mgy), water introduced for the first time in mining, milling and processing operations regardless of quality or source, within scope of the Bureau of Mines survey of water use in the nonmanfacturing mineral industry in 1962, was slightly more than one-half that of fresh water (517,858 mgy), suitable for cooking and drinking. The remainder (417,849 mgy) was primarily low-quality water not suitable for domestic use but not saline, and saline water (94,094 mgy) containing 1,000 ppm or more dissolved solids. Twenty-four percent of the total new water, 51 percent of the total discharge, and 75 percent of the total recirculated water was treated. Of the total quantity of water treated, 12 percent was new water, 83 percent was recirculated, and 5 percent was discharged water. The major methods of treating water were pH control (33 percent), settling (21 percent), bactericide (14 percent), and chlorination (11 percent). Most new water treated was subjected to filtration, settling, or bactericide treatment, whereas recirculated water was subjected to pH control and settling. The major discharge treatment was settling.

The Bureau of Mines, through its Industrial Water Laboratory, provides consulting boiler-water service to Federal agencies operating heating and power plants and financing and requesting this service (*5*). Each year 13,000 to 15,000 water-condensate samples are analyzed from more than 10,000 boilers. These analyses are helpful in spotting and correcting corrosion problems in boilers and condensate return lines.

Disposal of radioactive liquid wastes from uranium mining and milling operations have not posed a major problem primarily because the operations are located in remote areas. Mine water generally can be safely disposed to ground water or to the streams. Waste liquids from milling are diluted and released to streams or to retention ponds from which they gradually seep into the soil. Research conducted by the Bureau of Mines on disposal of radioactive waste from uranium mills indicated that the problem could be minimized by reuse of the waste milling solution, erasing the need for disposal of the liquid waste.

Most organic sewage wastes are treated by biological oxidation methods through which the organic material is ponded and attacked by biological organisms and reduced largely to gases, water, and sludge. Chemical and mineral substances on the other hand often require special chemical techniques in order to neutralize, precipitate, collect, or drive off the waste substances. Each industry has its own waste-disposal problem. Wider dissemination of knowledge and techniques in handling chemical and mineral wastes would be of value not only in controlling chemical wastes but also in recovering valuable mineral and chemical substances otherwise lost.

Wastes of the mineral industry are a special problem in many areas. In addition to acid-mine water, oil well brines are often a disposal problem. All wastes, however, should be examined closely for values which may readily be recovered. The recovery of iodine from oil-well brines is one example.

Cloud seeding to induce rainfall is practiced on a commercial basis in some areas. One procedure consists of burning coke impregnated with sodium iodine. The iodine particles carried upward with the hot gases act as nuclei for the condensation of moisture from rain clouds. Other procedures involve seeding with silver iodine, dry ice, or salt. The main problem in dry areas is to find clouds in the proper stage of supersaturation so that the addition of nuclei will cause rainfall.[3]

In 1934 Harold Urey discovered that the molecules of pure water contained, besides the common atoms of hydrogen and oxygen, an unusual type of hydrogen atom that was twice as heavy as the common variety. This isotope

[3] Committee print 22 (*32*).

of hydrogen, subsequently named deuterium, has an atomic weight of 2 and resembles hydrogen in many ways, combining with oxygen to form the compounds D_2O or heavy water.

The freezing and boiling points of D_2O are 3.8° and 1.4° C higher, respectively, than those of ordinary water (*6*). Besides being slightly more viscous than water, D_2O apparently is not used by plants or animals as readily as ordinary water. Many will die of thirst when supplied exclusively with it.

The largest use of heavy water is as a moderator in nuclear reactors, but it is also employed as a tool in theoretical research. If the less reactive deuterium is substituted for hydrogen in certain compounds, altered chemical properties, from which molecular structure may be studied, may result.

Heavy water may be produced in several ways. In one procedure deuterium is obtained from hydrogen gas by liquefying the gas and fractionating the liquid. Ordinary hydrogen molecules tend to boil off first. The resulting deuterium is reacted with oxygen to produce D_2O. The D_2O content of ordinary water may also be increased by electrolysis and by fractionating steam. To produce heavy water by these processes, large quantities of hydrogen, steam, or cheap electric power are required. It is economical, therefore, to build heavy-water plants in connection with plants that utilize large quantities of hydrogen or steam.

In addition to ordinary hydrogen and deuterium a third isotope of hydrogen, tritium, may be found in water. This material is of great importance in connection with the hydrogen bomb. Three isotopes of oxygen, O^{16}, O^{17}, and O^{18}, are also found in water. While tritium and O^{18} are present only in minute traces, deuterium and O^{17} average 200 and 1,000 parts per million, respectively. These 6 isotopes combine to form 18 different substances that may be found in water (*6*).

Both deuterium and tritium present in water are of great importance in studies of the controlled fusion reaction as an energy source. Although technical problems involved in achieving a fusion reaction with deuterium are more difficult than those raised by the use of tritium, the greater abundance of deuterium rules in favor of the latter.

USES

Water uses are classed as withdrawal and nonwithdrawal and consumptive and nonconsumptive. Domestic, municipal, irrigation, waterpower, and industrial uses are classed as withdrawal uses, as for these purposes the water must be pumped from the ground or diverted from a stream, lake, or reservoir. On the other hand, navigation, waste disposal, recreation, and conservation of wildlife are examples of nonwithdrawal uses. Water that is evaporated or incorporated into a product is said to be consumed or to be used consumptively.

The water withdrawal pattern for three selected years, 1950, 1955, and 1960, is shown in table 3 by the primary withdrawal uses, rural, public supplies, self-supplied industrial, and irrigation (*20*). Including conveyance losses, water used in irrigation in 1960 was the same as that for 1955. The quantity of water withdrawal for industry (self-supplied) increased substantially in 1960 and represented more than one-half of the total for all uses. Although it accounted for only 9 percent of the total water withdrawal, water supplied to the rural and municipal (public supplies) domestic users continued its increasing trend.

TABLE 3.—*Water withdrawal pattern 1950, 1955, and 1960, in the United States* (*20*)

Uses	Water withdrawal (billion gallons per day)			Percent increase, 1955 to 1960
	1950	1955	1960	
Rural	3.6	[1] 3.6	3.6	
Public supplies	14	17	21	24
Self-supplied industrial	77	110	140	27
Irrigation:				
Excluding conveyance losses	79	81	84	4
Including conveyance losses	[2] 110	110	110	
Total, all uses:				
Excluding conveyance losses	174	212	249	
Including conveyance losses	205	241	275	14
Waterpower	1,100	1,500	2,000	33

[1] Revised.
[2] Estimated.

Data in table 4, from the Bureau of Mines canvass of water use in selected segments of the mineral industry in 1962, show that seven industries accounted for 91 percent of the total water usage in that part of the mineral industry covered by the survey. These industries were natural gas processing, phosphate rock, sand and gravel, iron ore, petroleum well drilling and secondary recovery, copper ore, and bituminous coal.

Of the total water used (excluding petroleum well drilling and secondary recovery), 6 percent was used in mining and transporting materials, 64 percent for processing (including natural gas processing), 3 percent for cooling and condensing, and 3 percent for miscellaneous uses such as boiler feed and sanitary purposes.

Mills, preparation plants, sand and gravel washing plants, and natural gas processing plants accounted for 58 percent of the total water usage, 68 percent of the water re-

circulated, and 32 percent of the new water required. Surface mines and associated mills utilized 28 percent of the total water used, 23 percent of the water recirculated, and 41 percent of new water intake. Underground mines and associated mills, chemical or solution extraction, petroleum well drilling and secondary recovery, and natural gas processing accounted for the remaining water usage.

The major users of water for mineral processing by industry include natural gas processing plants and the phosphate rock, sand and gravel, iron ore, copper ore, and coal. Beneficiation methods, such as flotation, jigging, heavy-media separation, and spirals, require large quantities of water.

Major mineral industry users of water in mining, were phosphate ore (transporting), gold (hydraulic stripping, mining, and washing of the placer gold gravels), sulfur (solution mining by the Frasch process), and salt (solution mining of underground salt beds), which together accounted for the more than 90 percent of the total water usage in mining.

Only a small part or 6 percent of the total water usage in the natural gas processing plants was new water; the remainder was recirculated water used to cool the fractionating towers. Water is used extensively in the petroleum industry for well drilling, pressure maintenance of the producing zone, and for secondary recovery of oil. Approximately one-third of this total water usage for petroleum well drilling and secondary recovery was measured as recirculated water; the remainder was new water that usually was not fresh.

The Bureau of Mines has conducted many research projects and has published numerous reports on the subject of water injection and water flooding to maintain underground pressures and for secondary recovery of oil. Although the quantity of water used for this purpose is relatively large, most of it is water pumped with and separated from the crude oil and is reinjected. It should be considered as a form of recharging the ground water reserves even though it is counted as a consumptive use.

Water is being used extensively in pipeline transportation of solid materials as slurry. Solids pipelines are nothing new because they were used in California during the gold rush and the first U.S. patent for pumping solids through pipes was issued in 1889. For short distances they are used extensively in mills and

TABLE 4.—*Water usage in selected segments of the mineral industry, 1962* [1]

[Million gallons per year]

Industry	New water	Water recirculated	Total water usage	Water discharged	Water consumed	New water per dollar value of production
Anthracite	16, 938	14, 930	31, 868	15, 585	1, 353	129
Barite	4, 855	6, 164	11, 019	4, 441	414	505
Bituminous coal	31, 814	138, 493	170, 307	26, 135	5, 679	26
Clays	7, 118	1, 639	8, 757	6, 282	836	39
Copper ore	81, 035	93, 590	174, 625	50, 707	30, 328	99
Gold	54, 566	4, 155	58, 721	53, 921	645	158
Iron ore	112, 575	139, 540	252, 115	105, 672	6, 903	183
Lead and zinc ores	22, 885	1, 865	24, 750	21, 350	1, 535	144
Lignite	18	18	36	8	10	181
Phosphate rock	117, 167	269, 342	386, 509	87, 186	29, 981	876
Potash-soda-borate	7, 325	35, 555	42, 880	4, 434	2, 891	42
Salt	28, 933	8, 809	37, 742	22, 012	6, 921	189
Sand and gravel	217, 601	122, 732	340, 333	206, 236	11, 365	283
Stone, crushed	50, 415	16, 028	66, 443	47, 037	3, 378	66
Stone, dimension	3, 207	502	3, 709	3, 079	128	36
Sulfur	17, 604	161	17, 765	12, 956	4, 648	169
Uranium-vanadium-radium ores	7, 243	1, 039	8, 282	4, 201	3, 042	54
Other metals and nonmetals	25, 201	27, 791	52, 992	22, 971	2, 230	102
Total, metals, nonmetals, and coal	806, 500	882, 353	1, 688, 853	694, 213	112, 287	(2)
Natural gas processing plants	102, 358	1, 606, 834	1, 709, 192	68, 658	33, 700	(2)
Petroleum well drilling and secondary recovery	121, 538	74, 112	195, 650	10, 961	110, 577	(2)
Total, petroleum and natural gas industries	223, 896	1, 680, 946	1, 904, 842	79, 619	144, 277	(2)
Grand total	1, 030, 396	2, 563, 299	3, 593, 695	773, 832	256, 564	(2)

[1] Data may be slightly different from those shown in vols. I and III of Minerals Yearbook 1963 because of rounding and minor revisions.
[2] Not applicable.

processing plants. For many years consolidated Coal Co. successfully operated the longest coal pipeline in the world—108 miles from Cadiz to Eastlake, Ohio, on Lake Erie. In mid-1963 the company placed the pipeline on standby and started transporting its coal by railroad cars when lower rates were offered. American Gilsonite Co. has now operated a 72-mile pipeline in Utah, transporting gilsonite from its mine to mill, for 6 years. The ore is also mined and hoisted hydraulically at this operation. In South Africa more than a dozen pipelines have transported uranium-bearing tailings over long distances since 1956.

Water is a vital raw material in economically mining and processing phosphate ore in Florida. New techniques in hydraulic transportation of phosphate ore by pipeline have been pioneered there. Hydraulic transportation, involving the use of about 360 gallons of water per ton of ore, provides a low-cost and effective method of slurrying, scrubbing, and transporting the ore to the processing plant. Processing this ore requires an additional 3,000 to 10,000 gallons of water per ton of the final product. Less than one-third of the total water used for mining and processing phosphate ore is new water; the remainder is recirculated water.

Exploration and development of natural steam for electric power generation has been extensive in the Western United States in recent years. From 1955 to 1962, approximately 40 wells were drilled in 15 California thermal areas for this purpose (*23*). Geothermal plants are competitive with conventional units. In 1963 a geothermal plant could produce electric energy for 6.70 mills per kwhr, compared with 6.96 mills for coal, 6.74 mills for oil, and 7.04 mills for gas. Potential for geothermal power exists in the Western United States. An economic evaluation of geothermal power was made by the Bureau of Mines (*16*).

In a study made in New Mexico under a grant made to the University of New Mexico by Resources for the Future, Inc., it was found that each acre-foot of water would generate $51 in gross State product if used in farming, $3,041 if used in municipal and industrial purposes, and $2,793 if used for a combination of industrial and recreation (*37*).

A Bureau of Mines study of the water use in the mineral industries of Arizona (*14*) showed that the mineral-product value of copper, lead, zinc, and byproducts was equivalent to $15.27 for each 1,000 gallons, or $4,980 per acre-foot, of new water and $26.29 for each 1,000 gallons, or $8,570 per acre-foot, of consumed water.

BYPRODUCTS

Sea water, certain natural brines, and geothermal steams contain various minor minerals which, under proper conditions, may be recovered at a profit. Among these are bromine, calcium chloride, iodine, and sodium and magnesium compounds. Others such as potash may be economically recovered in the future. Various methods have been suggested for recovery of minerals from sea water (*7*, *28*).

Recent studies (*11*, *18*) were made on the minor elements, dissolved elements that do not generally exceed 1 milligram per liter, in natural water, and chemical data for the river and lake waters of the United States. The principal bulk of dissolved constituents in natural water consists of soluble products of chemical weathering and soil formation.

ALTERNATE MATERIALS

In most populous areas of the earth, water is so low in cost that substitution on a large scale is uneconomic. In areas of water shortage, low-quality water is often used for certain purposes in place of naturally fresh water. For example, sewage effluent is used in some areas for irrigation and industrial uses. Sea water is also used for cooling purposes by plants near the coast and for waste disposal aboard ships. In general, treated and reused water is thought of as the principal substitute for naturally fresh water. However, the trend in alleviating perennial water shortages has been toward importation of high-quality water from distant sources rather than toward substitution.

Air is used for cooling purposes in place of water and to remove heat from water. Air also takes the place of water in classifying and cleaning certain minerals and other commodities in the process called "dry blowing."

For certain specific purposes, such as the cooling of engines for operation at subfreezing temperature, ethylene glycol and alcohols are used in place of water. Mercury vapor has been used in place of steam in turbines designed to operate at high temperatures. Oil has been suggested as a substitute for water in grinding cement materials prior to clinkering.

SECONDARY SOURCES AND RECOVERY

Sewage effluent is used in many areas of the world for the irrigation of certain crops. Not only the water content but also a portion of the nitrogen content of the effluent is believed to be utilized by the crops.

In Baltimore, sewage effluent is utilized by the Bethlehem Steel Co. in the plant for nonsanitary purposes (*15*). The effluent requires no treatment except chlorination and settling.

The use of treated sewage effluent by oil companies for general plant use and for water injection in secondary oil recovery has also been described in many journal articles (*21*, *27*). These are only four examples of many instances where reclaimed sewage is employed.

RESERVES

An inventory of the world's total water reserves and potential resources available within the earth's hydrosphere shows that the overwhelming amount, an estimated 1,060,000 billion acre-feet or 32 times that of fresh water, is in the oceans. This water is presently usable as a transportation and recreation medium, as a natural source of food and minerals (sodium chloride, potash, and magnesium), and in industrial plants. If the oceans could be economically desalted and suitable disposition made of the removed minerals, the supply of fresh water would be virtually inexhaustible. Of the 33,016 billion acre-feet of fresh water in the inventory, 24,668 billion acre-feet or 75 percent is in polar ice and glaciers, and 8,213 billion acre-feet or 25 percent is ground water. All other forms of fresh water in lakes, rivers, soil, plants, animals, and the atmosphere are 135 billion acre-feet or less than 0.5 percent of the total amount of fresh water. Annual precipitation on land is 89 billion acre-feet and annual stream runoff is estimated at 28.5 billion acre-feet.

CONSERVATION

The greatest consumption of water is in irrigation because up to two-thirds of the water used is evaporated. Very little can be done to reduce this water loss; however, losses due to leaks in reservoirs and conduit systems and to phreatophytes are minimized by proper surveillance.

It has been estimated that in the arid and semiarid regions of the Western States phreatophytes waste more than 25 million acre-feet of water annually. Phreatophytes are plants that depend upon ground water for their water supply and that have low economic value. The water they use and return to the atmosphere without substantial benefit to man is defined as consumptive use. In the interest of conserving water to meet an ever-growing demand, more attention has been given to the phreatophyte problem (*25*, *26*).

Water evaporated annually from larger lakes and reservoirs having a combined area of 11 million acres is estimated to exceed the total water withdrawal for public supplies. Farm ponds, which are shallow and relatively warm, are more subject to evaporation loss than the deeper lakes and reservoirs. Loss due to seepage from small ponds and reservoirs has been estimated at three to six times the evaporation loss. However, seepage losses are potentially recoverable as ground water.

The water loss by evaporation from reservoirs and ponds is reduced by maintaining an adequate depth-to-surface-area ratio, thus minimizing the temperature rise. A film of hexadecanol (cetyl alcohol) spread on the water surface also retards evaporation.

Industrial water applications offer many opportunities for conservation. Elimination of leaks in conduit systems and use of shutoff valves to control unnecessary flow reduce waste. Greater reuse of water entails many problems associated with water quality, which usually deteriorates with each reuse.

A western steel firm conserves water by progressive reuse in the several processes of the operation. After water is used for the highest quality needs, a part of it is passed on to the next process that can use a lower quality water; the rest, along with new makeup water, is recirculated. Consequently, this plant consumes only 1,100 gallons of water per ton of steel, compared with the industry average of 65,000 gallons per ton of finished steel. Problems associated with the buildup of organic slimes in recycled cooling water have been attacked by using additives to destroy the organisms and eliminate corrosion caused by their waste products.

SOURCES OF STATISTICAL INFORMATION

Data on water use in selected nonmanufacturing segments of the mineral industry in the United States in 1962 were collected by a national survey conducted by the Bureau of Mines during 1963. Included in the survey were operators of metal and nonmetal mines, mills, and quarries; coal preparation plants and associated mines; petroleum-well drilling and secondary recovery, and natural gas processing plants. Metal smelters and refineries and cement and lime plants were excluded because they are classed in the manufacturing industries ordinarily canvassed by the Bureau of the Census. Stockpile and assessment work operations, natural brine operations, and coal mines without preparation plants were excluded to limit the size and complexity of the canvass and because it was concluded that together they constituted less than 1 percent of the total water

use in the mineral industry within the scope of the canvass. Recycled solvents such as leaching and cyanidation solutions also were excluded.

Primary producers of petroleum and natural gas were excluded because the water usage in these sectors was considered to be relatively small. Petroleum refineries were excluded because they are classed as manufacturing and not in the Bureau of Mines canvassing scope and because recent water-use surveys have been conducted by other Federal agencies and industry associations. Only the contract well-drillers were canvassed because they accounted for about 95 percent of the wells drilled for the petroleum and natural gas industries. The data collected from the contractors were expanded to cover the total footage drilled by contract and by oil and gas companies and operators.

More detailed data from this canvass on quality and source of water, new-water intake, and total water usage by major segments of the mineral industry were published in the Bureau of Mines Minerals Yearbook, 1963 (*17*). In addition, two proposed Bureau of Mines Information Circulars reporting on this canvass are under preparation; one, by Alvin Kaufman, will place emphasis on the water use in the metals, nonmetals, and coal components of the mineral industry, and the other, by Paul M. Buttermore, on the petroleum and natural gas industries. It is anticipated that a similar survey will be conducted by the Bureau once every 5 years to determine the trend of water use in the mineral industry.

WITHDRAWALS, REQUIREMENTS, DISCHARGE, AND CONSUMPTION

Water withdrawals and water consumed in 1960 are shown by water-use regions in table 1. Total withdrawals of 266 bgd in 1960 were more than 50 percent of the estimated dependable supply of 515 bgd in 1980. However, water consumed, 60 bgd, was only 22 percent of the total withdrawals in 1960.

United States water requirement for all uses for 1954, with predictions for withdrawals and consumption for 1980 and 2000, as given in the final report (*31*) of the Senate Select Committee, are shown in table 5. The streamflow in the United States in 1954 was about 1,100 bgd. On an anual basis, the Nation's streamflow has ranged from 50 percent of the average during periods of drought such as that during the 1930's, to nearly 140 percent of average during periods of excess precipitation. Withdrawal of 300 bgd in 1954 was 27 percent of the streamflow in that year. This figure is substantially higher than published estimates by the Federal Geological Survey for 1955 and for 1960 (table 1) because it was computed on the assumption that the optimum amounts of water for irrigation are made available to the growing plants; whereas, in actuality, substantial shortages were felt in 1954.

TABLE 5.—*Water requirements, 1954, 1980, and 2000, for withdrawals and consumptive uses or depletions from streamflow in the United States* [1]

[Billion gallons per day unless otherwise stated]

Purpose	1954				1980				2000			
	Gross withdrawals		Net consumption		Gross withdrawals		Net consumption		Gross withdrawals		Net consumption	
	Quantity	Percent of total	Quantity	Ratio of consumption to withdrawal (percent)	Quantity	Percent of total	Quantity	Ratio of consumption to withdrawal (percent)	Quantity	Percent of total	Quantity	Ratio of consumption to withdrawal (percent)
Division:												
Irrigation	176.1	59	103.9	59	167.0	30	104.5	63	184.5	21	126.3	68
Municipal	16.7	5	2.1	13	28.6	5	3.7	13	42.2	5	5.5	13
Manufacturing	31.9	11	2.8	9	101.6	18	8.7	9	229.2	26	20.8	9
Mining	1.5	(2)	.3	20	2.7	(2)	.6	22	3.4	(2)	.7	21
Steam electric power cooling	74.1	25	.4	.5	258.9	47	1.7	.7	429.4	48	2.9	.7
Total	300.3	100	109.5		558.9	100	119.3		888.4	100	156.3	
Onsite uses:												
Watershed improvement programs							4.0				7.0	
Swamps and wetlands for wildlife							66.7				89.9	
Total							70.7				96.0	
Grand total							190.0				253.2	

[1] Based on Resources for the Future, Inc., medium projects and in (*31*); data may not add to totals because of rounding.
[2] Less than ½ percent.

Demands are projected by the Senate Select Committee on National Water Resources to increase to 559 bgd or 51 percent of the streamflow by 1980 and to 888 bgd or 81 percent of the streamflow in the year 2000. These withdrawals or demands must be supplied through an expansion in the water resources development program. However, most of the water withdrawn is returned to the streams and can be reused many times, provided steps are taken to maintain its quality. Consumptive uses or losses for the various purposes, as shown in table 5, ranged from 59 percent of the water withdrawn for irrigation down to one-half of 1 percent for steam-electric power cooling. Water withdrawals for irrigation was 59 percent of the total withdrawals in 1954 compared with a projected 21 percent in the year 2000, while withdrawals for steam-electric power cooling was 25 percent of the total in 1954 and is expected to comprise 48 percent of the total in 2000. With anticipated increased evaporation and transpiration losses due to watershed, swamp, and wetland improvement programs, the total of national consumptive uses and depletions is projected to 190 bgd or 17 percent of the available streamflow in 1980 and 253 bgd or 23 percent in 2000.

Water requirements for 1954 and 1959 and projected requirements for 1980 and 2000 for principal water-using manufacturing industries, accounting for 66 percent of the total for all manufacturing in 1954 and 81 percent in 1959, as shown in the final report (*31*) of the Senate Select Committee, are shown in table 6. Projected total requirements for these industries for 1980 are nearly three times the 1959 requirements and for the year 2000 are more than six times that for 1959. Of these industries, chemicals has the greatest projected increased water requirements; by the year 2000 the chemicals industry will require 48 percent of the total water used by these industries and require more than nine times as much water as it did in 1959. Of the six principal water-using manufacturing industries shown in table 6, that represented 81 percent of the total manufacturing industries in 1959, four—iron and steel, chemical, aluminum, and copper, which represented 72 percent of the total manufacturing reported in table 4—are related to the mineral industry.

Special studies have been made and reports published on the water requirements of selected mineral industries; including the mining and milling, smelting, and refining operations; for copper (*24*), aluminum (*8*), and carbon black (*9*).

In table 4 data are shown for total water intake, recirculated, usage, discharged, and consumed at selected nonmanufacturing segments of the mineral industry in 1962 that were covered by the Bureau of Mines canvass. Of the total water usage in these metal, nonmetal, coal, natural gas processing, and petroleum well drilling and secondary recovery operations, 29 percent was new-water intake and the remainder was recirculated or reused water. Of the new-water intake, 75 percent was discharged or returned to the streams or the ground for reuse and the remainder was consumed through evaporation or shipped in the product. The metals, nonmetals, and coal industries as a group accounted for 47 percent of the total water usage, natural gas processing for 48 percent, and petroleum well-drilling and secondary recovery for the remaining 5 percent. The metals, nonmetals, and coal industries as a group discharged 89 percent of the total water discharged and consumed 44 percent of the total water consumed in those segments of the mineral industry covered by the canvass. Petroleum well-drilling and secondary-recovery operations consumed most of the remaining total water consumed.

TABLE 6.—*Water requirements, 1954, 1959, 1980, and 2000, principal water-using manufacturing industries* [1]

[Billion gallons per year]

Water intake by industry	1954		1959		1980		2000	
	Quantity	Percent of total	Quantity	Percent of total	Quantity	Percent of total	Quantity	Percent of total
Iron and steel	2,812	36.6	3,500	35.7	7,124	26.8	12,827	20.8
Chemical	2,380	30.9	3,210	32.7	10,800	40.7	29,700	48.2
Pulp and paper	1,607	20.9	2,140	21.8	6,893	26.0	16,173	26.3
Food	590	7.7	630	6.4	1,000	3.8	1,500	2.4
Aluminum	263	3.4	278	2.9	605	2.3	1,139	1.9
Copper	42	.5	49	.5	114	.4	247	.4
Total	[2] 7,694	100.0	[2] 9,807	100.0	26,536	100.0	61,585	100.0

[1] Based on Resources for the Future, Inc., median projections and on (*31*); data may not add to totals because of rounding.
[2] Represented 66 percent of the total for manufacturing industries in 1954 and 81 percent in 1959.

The source, adequacy, requirements, treatment, costs, reuse, and disposal of water in Arizona mineral industries was described in a report by the Bureau of Mines (*14*). Detailed schematic flow diagrams were shown for uses of water at many of the operations. Total new water required by major Arizona mineral industry operations in 1960 was 27,995 bgy, of which 14,205 bgy or 50.7 percent was consumed. Similar studies are being conducted in the States of Nevada, New Mexico, Wyoming, and Montana and in the Missouri River basin area of northern Missouri and Kansas.

Results were reported on a survey made of the industrial wastes of mineral origin, water requirements, treatment of wastes, and water-treatment practices of meal-processing and various other industries in the Missouri River basin of Kansas and Missouri (*12*, *36*).

GOVERNMENT PROGRAMS

The importance of national water resources problems has been recognized by Federal Government administrators for many years, and many bodies, commissions, and committees have been established to study the Nation's water supply and needs. Among bodies concerned principally or in part with water are the President's Water Resources Policy Commission established in 1950 and followed in rapid succession by the President's Materials Policy Commission, the House Subcommittee to Study Civil Works, the Missouri Basin Survey Commission, the Commission on Intergovernmental Relations, the Commission on Organization of the Executive Branch of the Government, the Presidential Advisory Committee on Water Resources Policy, and the Senate Select Committee on National Water Resources.

The Senate Select Committee on National Water Resources was established in 1959 to study the relation of water resources activities in the United States to the national interest, and the extent and character of water resources activities, both governmental and nongovernmental, that will be required to take care of needs for water for all purposes between that date and 1980. The published series of 32 committee prints (*32*), on the studies undertaken by and for the committee, comprise one of the most comprehensive reviews and forecasts of water-resources development in the United States ever assembled. The Bureau of Mines contribution to this Senate Select Committee study was published as Committee print 8. It includes information on water use in the mineral industry for 1954 and 1958 and projections for the years 1980 and 2000. The data for the water requirements, source, and discharge of water in the mineral industry were based on figures from the Bureau of the Census canvass of the mineral industries in 1954 conducted in cooperation with the Bureau of Mines and on figures from a Bureau of Mines canvass in 1958.

The final report (*31*) of the Senate Select Committee summarized the findings of the hearings, studies, and reports as published in the 32 committee prints and presents the committee's conclusions and recommendations for meeting growing demands on the Nation's water resources in the most efficient manner consistent with accepted public aims.

As a result of the committee's recommendation for a coordinated Federal Government scientific research program on water, the Federal Council for Science and Technology established a Task Group on Coordinated Water Resources Research to make a study. This task group prepared a comprehensive statement of the objectives and activities of all Federal agencies, comprising 5 departments and including 22 bureaus or equivalent units and 3 independent agencies, engaged in water resources research programs (*13*).

In 1952 the Office of Saline Water (OSW) was established in the Department of the Interior under the Saline Water Act to investigate and evaluate problems relating to large-scale desalting of saline water. In 1955 the Saline Water Act was amended and in 1961 the Anderson-Aspinall Act was passed, both of which continued and expanded the work of the OSW.

The Office of Water Resources Research was established in July 1964 by the U.S. Department of the Interior to administer the provisions of the Water Research Act of 1964, which authorizes annual grants to the State water resources research centers. A major aspect of the Office of Water Resources Research is a continuing program of grants to aid specific water resources research at land-grant universities.

PRICES

Prices paid for water vary widely, depending on the area and type of use. The estimated national average value of water was $135 per acre-foot, or 40 cents per 1,000 gallons. Conventional water costs ranged from 20 to 75 cents per 1,000 gallons. According to OSW the cost of converting sea water to fresh water in 1963 ranged from $1 to $1.50 per 1,000 gallons, compared with $4 to $5 in 1952. Two major factors in the cost of converting water are size of plant and cost of heat. Studies made by OSW indicated that the optimum plant size is about 25 to 30 million gallons per day and that using waste heat from an existing powerplant or building a combination powerplant and waterplant may

make this low-cost converted water competitive with high-cost conventional water in the near future.

Cost for new water at 14 mineral industry operations in Arizona, as reported (*14*) by the Bureau of Mines, ranged from 1.0 cent to 57.7 cents per 1,000 gallons, with an average of 12.5 cents, including power, labor, and supplies costs. Recirculation costs for power, labor, and supplies at three copper operations ranged from 1.0 cent to 1.8 cents per 1,000 gallons.

AEC operated the Savannah River heavy water plant, Aiken, S.C., at one-third capacity throughout 1964. Reevaluation of the service life of the plant's process equipment resulted in cost reductions that permitted a 12.5-percent decrease in the heavy water price to $24.50 per pound. Sales to U.S. customers during 1963 increased to over 4,000 pounds—about 1.5 times the 1962 sales. Foreign shipments totaled 54 tons of heavy water.

Heavy water was also available for leasing by foreign governments for 5-year periods or for the duration of bilateral agreements. Annual rental based on 4.75 percent of the purchase price of the water was charged.

RESEARCH

Salt water is more than 30 times as abundant as fresh water in the earth's hydrosphere and covers more than two-thirds of the earth's surface. Making use of the salt water to produce fresh water may be one of the means of satisfying the ever-increasing world's water demands. Many groups and organizations in the United States, governmental and otherwise, are interested in saline-water conversion research and development. The State of California has a sea-water conversion project, with the research being carried out at the University of California. Federal agencies having particular interest in saline-water conversion include the Departments of the Interior and Defense, AEC, and the Office of Emergency Planning. In addition, there is worldwide interest; extensive developments have been made in the Netherlands, Great Britain, and France. Some research on saline extraction has been reported in Spain and Italy. Saline-water research and development activity also has been reported in the U.S.S.R., Japan, Northern and Southern African countries, Australia, and Israel.

Scientific and technical activities in saline-water conversion range from basic research to demonstration and commercial plants. Now more than 25 mgd of fresh water is being produced from saline and brackish waters in large plants in various parts of the world. Most of it is produced from sea water, using several methods of distillation. The remainder is obtained by using electrodialysis processes on brackish waters. The largest sea-water distillation capacities are in Kuwait, on the Persian Gulf, and in Aruba and Curacao, in the Caribbean. Two of the newest plants, the largest saline-water distillation plants in the United States, are the OSW 1-mgd plants at Roswell, N. Mex., and Freeport, Tex. One other built at San Diego, Calif., was moved to the U.S. Naval Base at Guantanamo, Cuba, and placed on stream in the early summer of 1964 to supply fresh water after the Cuban Government had cut off the supply from Cuban sources. A new plant is being designed for the San Diego site. Large electrodialysis plants for brackish waters are at Bahrein in the Persian Gulf; Welkom, South Africa; Buckeye, Ariz.; and the OSW plant at Webster, S. Dak.

Fourteen scientific papers given at two symposia on saline-water conversion sponsored by the American Chemical Society, one in St. Louis, Mo., in 1961 and the other in Washington, D.C., in 1962, were published (*3*). This report is a sequel to a publication (*2*) by the same society in 1960 that was widely read and that reportedly stimulated new interest in the saline-water conversion program.

As part of its effort to promote and assist less developed countries towards self-sustaining growth and, more particularly, under its program for water resources development, the United Nations Secretariat surveyed the economic and technical aspects of salt-water conversion (*29*). While its survey showed that the known processes yield an expensive fresh-water product, it revealed many interesting possibilities of application even at present costs. Desalting, it appears, can already make a valuable contribution to economic development and may become an important feature of international cooperation.

The 1963 research and development programs on saline-water conversion conducted by OSW (*35*) took major steps toward lowering the cost of producing fresh water from salt water. OSW assumed a major role under the aegis of the International Atomic Energy Agency in worldwide efforts to use nuclear power as a source of heat for desalting. Important applied research facilities began operating at the new OSW Research and Development Test Station at Wrightsville Beach, N.C. Increased emphasis was placed on basic research on water. Favorable results were reported on two OSW preliminary appraisal studies, a nuclear-fired combination electric power and sea-water desalting plant to provide fresh water for the Florida Keys at an economically competitive price, and an oil-fired combination electric

power plant and desalting plant to serve municipal requirements at Tijuana, Mexico.

Five demonstration plants to convert saline water to fresh water have been completed by OSW to serve as pilot operations to test the various distillation processes. The first plant to be built by OSW is at Freeport, Tex., and uses the multiple-effect long-tube vertical-distillation process to produce 1 mgd of fresh water from sea water. It has 12 effects and the evaporators are of a falling-film type. A multistage flash-distillation process (36 flashing stages) with a capacity of 1 mgd of fresh water from sea water was the OSW second plant. It was built at San Diego, Calif., but was moved to the U.S. Naval Base, Guantanamo Bay, Cuba. A third plant, operating on brackish well water, using the electrodialysis membrane process, and having a fresh-water output of 250,000 gallons per day, was built by OSW at Webster, S. Dak. The fourth demonstration plant was completed in mid-1963 at Roswell, N. Mex., rated at 1 mgd of fresh water and using the force-circulation vapor-compression process for converting highly brackish water to fresh water. A fifth sea-water conversion pilot plant was completed by OSW in 1964 at Wrightsville Beach, N.C. It uses the freezing process and has a daily fresh-water output capacity of 200,000 gallons. The intended purpose of the plant is to supply fresh water to the city of Wrightsville Beach to augment its present limited sources of natural fresh water. Data obtained from the five OSW pilot operations are providing information that is being studied and evaluated to form the basis for the design of larger and more efficient plants.

In December 1964 a feasibility study was begun that was sponsored jointly by the Metropolitan Water District of Southern California, the U.S. Department of the Interior, and the AEC for a dual-purpose electric power and water-desalting plant capable of producing up to 150 mgd of pure water.

Flood-control, deep-well pumping, and drainage-alleviation projects relating to anthracite coal resources were continued in 1964 by the Bureau of Mines. The program, has implemented Federal and State anti-stream-pollution activities, assisted in conserving natural resources, and enhanced the economy of the anthracite-producing region. The problems and reports written on acid-mine drainage, which have been studied for the past 40 years, were summarized in two Bureau of Mines publications (*4*, *19*).

Acid-mine drainage control research projects in bituminous coal mines were continued by the Bureau of Mines in 1964. The projects comprised (1) a cooperative study with the Ohio River Valley Water Sanitation Commission on the assessment of the value of mine sealing as a means for reducing the efflux of acid mine water from abandoned above-drainage coal mines; (2) a cooperative pilot study with the U.S. Department of Health, Education, and Welfare, Public Health Service, on the application of the best known corrective measures to a watershed now being polluted by acid mine water; and (3) a laboratory study to determine the conditions required for the formation of acid in mine drainage, obtain more complete knowledge on the mechanism of the chemical and biochemical reactions that produce acid mine water, and explore physical, chemical, and biochemical process for its control.

Fundamental mine-hydrology studies are being made by the Bureau of Mines. These studies are intended to develop methods, techniques, instruments, and engineering principles for defining mine-drainage problems prior to the development of underground mines and for controlling the drainage of water in mines.

The Bureau of Mines has conducted extensive experimental work and research on hydraulic mining of both pitching and flat-lying bituminous coalbeds to determine the economics, practicability, safety, and productivity of this method of mining and on hydraulic transportation of coal. Numerous reports have been published giving results of such work.

Material, usually mill tailing, is extensively being hydraulically emplaced as stope fill in underground mines. Research is being conducted by the Bureau to develop the design principles for optimum use of hydraulic backfill as a means of ground support in mines under various conditions of geology, mining methods, and stresses acting upon the mining area.

Heavy water (D_2O), water incorporating deuterium instead of normal hydrogen, absorbs fewer neutrons than ordinary light water. Reactors moderated with heavy water can operate efficiently on natural or slightly enriched uranium fuel. Different types of heavy-water-moderated reactors have been studied in the United States for several years. Recent studies by du Pont and Combustion Engineering made for AEC have shown that the concept has good potential for reduction in unit-power costs in sizes of 500,000 electrical kilowatts or higher. The concept also has a potential application in the production of large amounts of heat for industrial processes such as desalting of sea water (*30*).

OUTLOOK

Continuing and expanded efforts will be required to develop and provide the United States with water in adequate quantity and of satisfactory quality from our finite limits of water supply to meet the ever-increasing needs. The demands of growing population, agriculture, and industry will press on the potential limits of the natural supply of water in certain areas.

The Nation's water resources are not uniformly distributed in all geographic regions. Substantial areas of the river basins in the western half of the United States already have a water shortage. Of the 22 water resources regions of the United States, full development of all of the available water resources in 5 of the western regions will be required by 1980 or earlier. By the year 2000, three more regions will be added to this list requiring full development of all available water resources. Continuation of growth of population and economic activities in these areas will pose many technical, legal, financial, and political problems involved in meeting future water needs. Solutions to such problems will require a major effort by Federal, State, and other agencies and the public, working in close cooperation.

As full development of water resources in a given area is approached, many changes in the utilization and management of water may be expected. Developing water resources to the fullest extent will be reflected in higher costs for water and in increased waste and sewage treatment. Control of pollution will become more stringent, and water conservation methods will be used more widely. Eventually it may be necessary to process all waste for disposal in streams so the effluent will meet rigid standards of purity.

Water will tend increasingly to be used where it will produce the greatest economic and social benefit. The value of manufactured goods produced with the use of 1,000 gallons of water is usually many times the value of agricultural products using the same quantity of water. On the other hand, the measurable values derived from water used in the maintenance of wetlands for wildlife habitat may be less than those derived from irrigating agricultural land.

Research will be continued to explore more of the physical and chemical properties of water in relation to its use, so that new sources of supply may be created from saline water and other sources. The problems of reuse of water will continue to be studied to the end that pollutants of all types can be controlled and safe standards of purity can be established and maintained.

National demands for water withdrawals for all uses were 300 bgd or 27 percent of the streamflow in 1954 and are projected to increase to 559 bgd or 51 percent of the streamflow by 1980 and to 888 bgd or 81 percent of the streamflow by 2000. However, most of the water is used and reused and returned to the stream and can be used by others, provided steps are taken to maintain the quality of the water returned to the streams.

Consumptive uses or depletion from streamflow, for the various purposes, range from about 60 percent of water withdrawn for irrigation down to a fraction of 1 percent of water diverted for steam-electric power cooling. Consumptive uses of 110 bgd or 10 percent of streamflow in 1954 are projected to 119 bgd or 11 percent of streamflow in 1980 and 156 bgd or 14 percent of streamflow by 2000. Additional consumptive losses from contemplated conservation practices for onsite water uses for watershed improvement and swamps and wetlands for wildlife programs raise the projected consumptive uses to 17 percent of the available streamflow by 1980 and 23 percent in 2000.

The principal factor responsible for the growing needs for water is the rapid gain in population and man's concurrent demand for an increased amount of goods and services requiring the use of water. The per capita use of municipal water, which has risen from an average of 108 gallons per day in 1950 to 134 gallons in 1960, is expected to reach 158 gallons per day by 1970. But of most importance is the increased water demand for steam-electric power cooling, manufacturing, irrigation, waste dilution, and the mineral industry.

The withdrawal of water for irrigation will continue to grow from 176 bgd of the 300 bgd total for all uses in 1954 to a projected 185 bgd of the 888 bgd total in 2000. However, from these figures it can be seen that irrigation is expected to represent a smaller part of the total withdrawal for all uses in the future, 59 percent of the total in 1954 compared with a projected 21 percent of the total in 2000. Steam-electric power cooling took 25 percent of the total in 1954 compared with a projected 48 percent of the total in 2000. Water withdrawals for manufacturing in 1954 were 11 percent of the total compared with a projected 26 percent by 2000.

Production of chemicals will take the largest share of the expected increase in future water requirements for the manufacturing industry. The manufacture of pulp and paper and food processing are also expected to take larger quantities of water as will the mineral-process-

ing industries of iron and steel, aluminum, and copper. Total water requirements for these six industries, which constituted 81 percent of the total water requirements for all of the manufacturing industries in 1959, are projected to 26,536 bgy in 1980 or three and one-half times that of 1959 and 61,585 bgy by 2000 or eight times the 1959 total.

The water requirements for the nonmanufacturing segments of the mineral industry, including metal and nonmetal mines, mills, and quarries, coal-preparation plants and associated mines, petroleum well-drilling and secondary recovery operations, and natural gas processing plants, are relatively small in comparison to the total water demand for the entire manufacturing industry. However, the requirements for new water by the mineral industry are expected to increase from 1,030 bgy in 1962 to more than 2,000 bgy (double that of 1962) in 1980 and more than 4,000 by the year 2000. To supply the total requirements of the mineral industry, a greater quantity of water will be recirculated or reused because the total water usage, which is the sum of new-water intake and water recirculated, is expected to be three times the 1962 figure of 3,594 bgy by 1980 and six times that of 1962 by 2000.

PROBLEMS

The primary and pressing problem for national water resource planners is one of providing an adequate quality and quantity of water at the time and place to meet the growing demands as the upper limit of potential supply from surface and ground sources is approached. Five major categories of effort are needed for meeting prospective demands on a long-range basis, so as not to inhibit national or regional growth, (*31*) as follows:

1. Regulating streamflow by the construction of surface reservoirs and watershed management.
2. Improving the quality of our streams by more adequate pollution-abatement programs.
3. Making better use of underground storage.
4. Increasing the efficiency with which water is used by elimination of wasteful practices, improved sewage-treatment methods, recirculation, increased irrigation efficiency, and substitution of air for water cooling.
5. Increasing the natural water yield by desalting, weather modification, and other artificial means.

The five demands listed above are complex, and solving the problems related to them is difficult and often creates other problems. Excess of water supply usually corresponds with cool rainy seasons, whereas the peak in water demand comes in hot, dry periods. Building reservoirs to store this excess water for use during the dry period creates other problems because the water may inundate towns, farmland, forests, mineral deposits, and historical and archeological sites. Evaporation from reservoirs is consumption and substantially reduces the benefits derived from such structures.

The most effective and economical methods for treating waterborne wastes, both organic and inorganic, must be determined so that the water will be suitable for reuse wthin a reasonably short period and the waste material will be converted into a usable or an inoffensive product. Under present practices biochemical action to remove organic wastes results in increasing concentrations of nitrates and phosphates. This in turn promotes the growth of algae blooms resulting in bad-tasting water and possible fish kills. If economical methods for recovering nitrates and phosphates from sewage-plant effluents were developed, not only would valuable fertilizer materials be produced but stream pollution would be reduced as well. Recent estimates are that by 1980 streamflow of satisfactory quality can only be maintained if the quantity of organic wastes removed from each gallon of municipal and industrial sewage is doubled. Chemical and radioactive waste removal also presents many problems. The cumulative effects on the potential water supply of certain chemical substances used as insecticides and herbicides is unknown, and standards for their removal remain to be formulated.

As the demand for water approaches the limit of supply, apportionment of water among the various users and for various purposes becomes very complex. An example of the complexity of water management is the fact that flood control requires an empty reservoir or one maintained at low level; hydroelectric power and municipal water supply require a reservoir maintained at high level, but with a water level that can be lowered as the water is needed; recreation and wildlife management require a reservoir with a relatively stable water level; and pollution abatement needs a reservoir that will stabilize streamflow in the various seasons of the year. Reconciliation of the demands for water for its many varied purposes requires careful evaluation in order to achieve the maximum benefits in the public interest.

Reuse of water tends to increase the concentration of pollutants. The effects of increased concentration of many pollutants and satisfactory control methods remain unknown. Temperature of the water may increase, causing

rapid growth of algae and other organisms which foul pipes and equipment and increase corrosion.

Large-scale pumping of water from aquifers often causes land subsidence which affects surface structures and may lead to compaction of aquifers, resulting in loss of their capacity for storing water. Lowering the water table by excess pumping near the ocean or other saline sources of water leads to contamination of the aquifer with salt water.

The water problems of the mining industries are varied. In water-short areas, obtaining an adequate supply of water of satisfactory quality for mining and metallurgical operations is a major problem. In other areas the flooding of mines by excess ground water and surface flow is equally serious. Disposal of oil-well brines and refinery wastes is a problem of the oil industry, and control of acid mine water from the coalfields is an important problem of the coal industry. Disposal of waterborne wastes resulting from metallurgical operations and from grinding, sizing, and cleaning minerals is a disposal problem of the mineral industry in general.

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YTTRIUM

By John G. Parker [1]

YTTRIUM is always associated with the rare-earth elements in nature, but pure yttrium compounds have been available only since 1947. Production of yttrium and yttrium compounds has been developed as a small part of the rare-earth industry. Monazite, xenotime, and euxenite concentrates are digested with acid or sodium hydroxide, and the yttrium and rare-earth elements separated as mixed insoluble oxalates, precipitated by varying the pH, or loaded in solution onto ion-exchange resin beds. The products are converted to oxides, halides, and other salts. When needed, further separations or purifications are made by solvent extraction or ion-exchange methods. Yttrium metal is produced by electrolysis or by reduction of the fluoride or chloride with calcium, lithium, or sodium.

The major commercial application for yttrium to date has been in devices used in microwave electronics. Very recently certain advances in laser technology and particularly in color television have been shown to depend upon yttrium usage. A potential large-scale use of yttrium materials may be in the production of ductile cast iron.

The prices of yttrium metal and compounds vary with the producers, the purity or grade of the product, and the quantities purchased. Yttrium oxide prices range from $45 to $500 per pound for material of 99 percent to 99.9999 percent purity. Yttrium metal—99.9 percent pure—is quoted at $208 per pound; an yttrium misch metal is quoted at $38 per pound.

Production of and research programs on yttrium have been sponsored mainly by government agencies.

The problems of yttrium production include the development of uses and demand, disposal of surplus quantities of yttrium materials held by government agencies, and incomplete knowledge on abundance and location of domestic resources.

BACKGROUND

Johann Gadolin, a Russian chemist, isolated a new "earth" or metal oxide in 1794 from a mineral found at Ytterby, Sweden. The mineral from which the earth was extracted was later named gadolinite in his honor. In 1797 Ekeberg suggested the name yttria for this compound which both he and Gadolin considered as an oxide of a single element. Subsequently, several independent investigators discovered a second oxide, which was named ceria. Still later, it was found that these two oxides were composed of complex mixtures of the oxides of a number of unknown elements. The presence of a number of rare-earth- and yttrium-bearing minerals which were early subjected to intense study has immortalized the name of the area in the names yttrium, ytterbium, terbium, and erbium. The extremely complex riddle presented by the chemical and physical nature of yttrium and the 14 naturally occurring rare-earth elements required over a century to solve, being studied by eminent chemists such as Berzelius, Crookes, Klaproth, Marignac, and Mosander. Large-scale separation of pure yttrium was not possible until 1947, however, at which time an ion-exchange process was developed by F. H. Spedding and his associates at Iowa State College.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Producers extract small quantities of yttrium in the processing of monazite and other rare-earth minerals. The companies identified most closely with some phase of yttrium recovery include: Rare Earth Division, American Potash & Chemical Corp., West Chicago, Ill.; Michigan

[1] Commodity specialist.

Chemical Corp., St. Louis, Mich.; Research Chemicals Division of Nuclear Corp. of America, Phoenix, Ariz.; and Vitro Chemical Co., Chattanooga, Tenn. Lunex Co., Pleasant Valley, Iowa, produces yttrium metal.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Yttrium, Y, atomic number 39, occurs between the elements scandium and lanthanum in group III of the periodic table. It is homologous with the rare-earth metals, its chemical nature and occurrence being so nearly like these elements that it is difficult to separate from them. Yttrium metal has a hexagonal close-packed crystal structure of 4.48 density to 1,490° C, just below its melting point of 1,509° C. It boils at 2,927° C and has a thermal neutron cross section of 1.3 barns per atom. Pure yttrium metal is ductile and has good resistance to atmospheric corrosion. Its chemical reactivity in ordinary environments, however, is increased greatly by the presence of other metals, particularly some of the rare-earth metals. Small quantities of dissolved oxygen, nitrogen, and fluorine make yttrium brittle. Pure yttrium metal is not attacked by molten uranium-chromium eutectic at 900° C and is immiscible, or nearly so, with a number of other molten metals such as tantalum and vanadium (*1*).[2]

Yttrium oxide, Y_2O_3, or yttria, has a cubic crystal structure, a density of 4.84, a melting point of 2,410° C, and a boiling point of 4,300° C. It is a poor conductor of electricity, is fairly stable in air, and is not easily reduced.

Companies designate as high-purity metal yttrium of 99.9 percent quality which may be purchased as ingots, crystal sponge, lumps, and turnings. Distilled metal of greater than 99.9 percent purity is also available. Yttrium oxide, with a purity up to 99.9999 percent based on rare-earth oxide (REO) content, is produced by the industry.

Analytical determinations are difficult to perform on mixtures of the closely similar yttrium and elements of the rare-earth group. In evaluating ores and concentrates, yttrium and the rare-earth elements present are precipitated in a group as oxalates which are then ignited to the oxides, weighed, and reported as REO. More accurate analytical methods must be based on physical properties of the elements, such as the average atomic weight of the mixed elements, the magnetic susceptibility, and methods using arc, X-ray, or atomic absorption data. Neutron activation is used to determine extremely small quantities of contaminating materials, and the inert gas fusion method has been used to accurately determine oxygen in yttrium and yttrium fluoride. The type and distribution of inclusions present in the metal may be determined by metallographic inspection of the microstructure.

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

TECHNOLOGY

Geology

Although yttrium is always found in nature with the rare-earth elements, it is said to be concentrated predominantly in the earth's crust as pegmatitic differentiates from granitic magmas, whereas rare-earth elements of the cerium subgroup occur mostly in differentiates from syenitic magmas. Some of the syenites, however, were calculated to contain about 8 grams per ton yttrium, and certain aluminum-rich schists contained almost twice that quantity (*10*). Despite the fact that yttrium is sometimes concentrated in notable quantities in apatite and garnet, more common yttrium-bearing minerals include xenotime, gadolinite, members of the euxenite-polycrase and fergusonite-formanite series, samarskite, yttrotantalite, yttrofluorite, and doverite. Monazite, with rarely up to 5 percent yttria, and bastnaesite, with seldom more than 0.1 percent yttria, are discussed in the chapter on rare-earth metals. Although they are low grade sources of yttrium, they have served as the principal source of byproduct yttrium because of the large quantities of concentrate processed and the relatively limited demand for yttrium.

Xenotime, essentially yttrium phosphate with erbium and other heavy rare-earth elements, contains from 50 to 68 percent REO. It is found almost invariably in small quantities with monazite in granitic and gneissic rocks and in stream and beach placers. Gadolinite, a complex beryllium-iron-yttrium silicate found in granite pegmatites, theoretically can contain about 48 percent REO usually 60 percent of which (nearly 30 percent of the mineral) may be Y_2O_3. Thalenite and yttrialite are other rare silicates rich in yttria. Minerals of the euxenite-polycrase and fergusonite-formanite series are multiple oxides containing columbium, tantalum, and from 16 to over 45 percent yttrium and other heavy rare-earth metals. Usually minerals of the euxenite-formanite series contain significant quantities of uranium and thorium. A mineralogical phenomenon, called the metamict state, is often characteristic of these multiple oxide minerals which have their crystalline structures disarranged by alpha radiation from the uranium, thorium, and other decay products.

Samarskite, yttrotantalite, and yttrofluorite are uncommon minerals containing from 6 to 17 percent yttria. Doverite, an yttrium fluocarbonate with about 45 percent REO, first reported from a Morris County, N.J. iron mine, has been considered by some researchers as an yttrian synchisite. This material may contain as much as 35 percent heavy REO, most of which is yttrium, with lesser quantities of the light REO. Apatite may contain significant quantities of yttrium and rare-earth elements substituted for calcium, a notable occurrence being its association with magnetic iron ore at Mineville, N.Y. Here the heavy subgroup is less than half the combined REO content, and Y_2O_3 may total several percent of the mineral.

Minerals containing yttrium and rare-earth elements are found disseminated and in veins in alkalic rocks, granites and syenites, granitic and syenitic pegmatites, gneisses, carbonatites, and contact metamorphic rocks. Some are concentrated in basic rocks, notably associated with magnetite. Fluvial and beach placer deposits, derived from primary deposits, are the main economic sources of yttrium. For example, monazite is now processed in Florida and xenotime was formerly extracted from a placer deposit at Aiken, S.C. Large placers in Idaho and Montana formerly were worked for their rare-earth and thorium contents. In Bear Valley, Idaho, alluvium washed down by streams from a deep regolith was deposited in placers worked for columbite, tantalite, and euxenite in the late 1950's.

In the United States, in addition to the rare-earth-bearing magnetite ores in New York and New Jersey, other notable bedrock occurrences are with thorite in mineralized shear zones in Precambrian metamorphic rocks of the Powderhorn district, and with thorium deposits in a Precambrian complex in the Wet Mountains area of Colorado. In Canada, yttrium has been derived as a byproduct from brannerite-uraninite ore found in the conglomerate type deposit of the Blind River, Ontario, area.

Mining and Beneficiation

Conventional methods employing suction and bucketline dredges are used to recover monazite, xenotime, and euxenite from beach sands and river gravels. Jigs are used to separate gravels and coarser materials and Humphrey spirals, sands. The bulk concentrate, called "black sand," is sent to a plant where it is subjected to magnetic and electrostatic separation to obtain the individual minerals. Wet magnetic separation is used to remove most of the magnetite and part of the ilmenite. After the residue is dried, it is passed over magnetic separators, using magnetic fields of varying strengths, to remove successively the remaining magnetite, ilmenite, and garnet.

It was reported that flotation with oleic acid was used for production of concentrate from the vein monazite deposit at Van Rhynsdorp, Republic of South Africa (*11*).

Processing

The recovery of yttrium requires complex chemical processing. Most rare-earth and yttrium concentrates are processed commercially by one of two methods, as described fully in the chapter on rare-earth metals. The general plan is to treat finely ground mineral concentrate with sulfuric acid or sodium hydroxide, separate rare-earth elements and yttrium from uranium and thorium, and then separate rare-earth elements from yttrium.

The most commonly used breakdown method for acid leachable minerals such as monazite and xenotime is digestion with hot concentrated sulfuric acid. More refractory minerals such as euxenite, fergusonite, and samarskite are fused first with sodium hydroxide to make them more soluble. Treatment by the sulfuric acid process entails reacting finely ground concentrate with hot sulfuric acid, dilution with cold water, and then any one of several methods to separate rare-earth elements and yttrium from thorium and uranium. For example, thorium, uranium, and a small part of the rare-earth elements are separated by neutralizing the solution to a pH of 1.0, most of the remainder of the rare-earth elements and yttrium are precipitated at pH 2.3, and the uranium and the rest of the rare-earth elements are precipitated from the filtrate at about pH 6. Another method entails precipitating thorium and rare-earth elements from diluted solution with sodium oxalate and converting the oxalate to hydroxide by treating with hot caustic soda (*11*). The hydroxides are heated to form oxides which are then dissolved in nitric acid, and the rare-earth and yttrium values are removed from thorium and cerium by solvent extraction with tributyl phosphate (TBP).

In the sodium hydroxide digestion of monazite, the reaction mixture is diluted and the sodium hydroxide-sodium phosphate solution filtered from the hydrous yttrium and rare-earth oxides, the hydrous oxide cake is dissolved in hydrochloric acid, and the thorium and uranium precipitated from the solution by raising the pH (*11*). After the crude thorium hydroxide is separated, the rare-earth metals and yttrium are precipitated from the filtrate by raising the pH further. In another method, developed for the treatment of xenotime, the

mineral concentrate is digested with hot sulfuric acid (*5*). The leachate from the digestion is then loaded onto cation exchange resin beds and eluted with ammonia-buffered ethylenediaminetetraacetic acid (EDTA) solution containing cupric ion which prevents precipitation of the insoluble EDTA on the resin bed. The yttrium and rare-earth metals are separated in different fractions of the eluant, precipitated as their oxalates, and then ignited to their oxides.

In the separation of yttrium and elements of the yttrium subgroup by large-scale ion exchange with EDTA and nitrilotriacetic acid (NTA), the use of Cu^{2+} and Zn^{2+} retaining ions facilitated redeposition of rare-earth ions on the resin bed in the column after they had been dislodged by the eluant from the resin phase (*9*). Ammonium and ammonium-hydrogen ions have been used alone or added to the copper retaining ion when separating yttrium under less acid conditions.

A hydroxyethyl EDTA, called HEDTA, used with a hydrogen-state resin bed, avoids the need for a heavy-metal retaining ion, is easily recovered from an aqueous solution, and can be recycled (*9*). Diethylenetriaminepentaacetic acid (DTPA) has been used at elevated temperatures to isolate yttrium in a pure state.

Solvent extraction is being used increasingly by industry. Its applications and advantages are mentioned in the chapter on rare-earth metals, but it can be used to isolate yttrium from rare-earth elements by employing two different solvent extraction systems (*7*). Yttrium and heavy rare-earth values are extracted from an acidified aqueous solution with dialkyl phosphoric acid (*8*). The resulting organic phase, rich in yttrium, was stripped by an aqueous mineral acid, and the yttrium subsequently was left in this aqueous strip solution after the other heavy rare-earth metal values were removed by a solvent such as trialkyl phosphate. Bureau of Mines researchers have recovered yttrium oxide from siliceous thorite ores of the Powderhorn area in Colorado by acid curing, baking, leaching, and solvent extraction with di-2-ethylhexyl phosphoric acid (D2EHPA) (*2*).

The fluoride and chloride of yttrium, from which the metal is won by metallothermic reduction, are usually prepared by reacting yttrium oxide with ammonium hydrogen fluoride or anhydrous hydrogen fluoride at elevated temperatures, or by mixing yttrium oxide, ammonium chloride, and hydroxylamine hydrochloride together and heating (*5*). Before employing metallothermic reduction, Bureau of Mines investigators purified yttrium halides by vacuum distillation. In laboratory-scale work, use of high-purity lithium or sodium as a reductant permitted 95 percent recovery of an yttrium sponge metal which was more than 99.8 percent pure (*6*). Massive yttrium metal has been produced on a commercial scale by the direct reduction of yttrium fluoride (YF_3) with calcium at high temperature in an inert atmosphere. More recently, in metallothermic reduction of the chloride with lithium or sodium, it was not necessary to heat the reactants as much as when using the fluoride. (*4*). Yttrium metal also has been produced on a large scale by reducing the fluoride with calcium, in excess, in the presence of magnesium. The resulting yttrium-magnesium alloy was heated in a vacuum to sublime the magnesium and residual calcium, leaving a metal sponge which was arc melted into ingots. Electrolysis may be used to electrowin yttrium metal from the oxide in a bath of fused alkali halide.

Recently the Bureau of Mines has electrowon yttrium from Y_2O_3 on an iron cathode using a fluoride electrolyte, thereby preparing a low melting alloy. Efforts were being made to coreduce iron-yttrium oxides to the alloy in a fluoride electrolyte. Yttrium was electrorefined and vacuum distilled, using a $LiCl\text{-}YCl_3$ electrolyte; solid state electrolysis was used to remove significant nickel, iron, and oxygen from yttrium metal bars.

Other refining methods include consumable electrode arc melting under vacuum and purification by high temperature distillation.

USES

The major and probably only commercial use of yttrium is in yttrium-iron garnets, called "yigs" in the electronics industry. These crystals, having the general composition $3Re_2O_3.5Fe_2O_3$ where Re is rare-earth elements or yttrium, serve as filters for selecting or tuning microwaves. Recently yttrium-aluminum garnets (yags), with low lasing thresholds and needing little cooling, have been used in lasers. Yttrium orthovanadate and yttrium oxide, both activated by europium, are two superior red phosphors said to provide high luminosity in color television tubes.

Other potentially important uses of yttrium, upon which significant research has been conducted, are as a structural metal in nuclear reactors because of its low thermal neutron cross section and relatively high melting point; as a hydride with superior thermal stability which makes it of value as a neutron moderator in nuclear reactors; as a scavenger and grain refiner in vanadium, and as a preventor of nitride formation and promoter of high temperature oxidation resistance in chromium; as corrosion-resistant metal pipe in fluoride processing; as a refractory oxide coating with good thermal

shock resistance; and, probably most significant, as an additive promoting the formation of nodular graphite in ductile cast iron.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Monazite and euxenite are usually recovered as byproducts from the processing of beach sands and river gravels for titanium minerals, zircon, columbite, gold, or tin. Since the Atomic Energy Commission (AEC) thorium procurement program ceased in 1959, the rare-earth elements and yttrium extractable from monazite have become more important to the industry than has the thorium. Euxenite, formerly processed primarily for its columbium-tantalum content and secondarily for uranium, thorium, and the heavy or yttrium subgroup elements, has not been mined domestically since the late 1950's.

ALTERNATE MATERIALS

Although research on yttrium has shown the potential value of the metal and its compounds for various applications, its most important use to date has been in components of microwave equipment. In this electronic field, especially as yttrium-iron garnets which have low electrical and low eddy-current losses, it has competed successfully with other cheaper, more plentiful materials such as the spinel-type of ferrite compounds. Yttrium oxide has been suggested as a refractory coating, but thorium oxide is a cheaper stable refractory oxide which, however, has poor resistance to thermal shock. Yttrium hydride, as a neutron moderator, must compete with standard moderators such as graphite, beryllium, and heavy water. Due to its low neutron cross section yttrium metal has received attention as a structural metal in nuclear reactors along with columbium and tantalum but zirconium, aluminum, and stainless steel are cheaper and are commonly used. The large scale usage of yttrium in the production of ductile iron is hindered at this time by the lack of satisfactory yttrium materials at generally acceptable low prices competitive with the commonly used nodularizers such as ferrosilicon-magnesium misch metal alloy or nickel-magnesium alloy.

RESOURCES

The consideration of yttrium as a mineral commodity separate from the rare-earth elements, with which it is always associated, has taken place only in the past 5 or 6 years. The most common rare-earth mineral, monazite, is a primary source of yttrium, and it may be considered as a byproduct of the recovery of cerium group metals which have had greater usage. Although the yttrium oxide contents of monazite from various localities sometimes differ greatly, the yttrium contents of 15 domestic monazites showed an average of about 2.5 percent of the total rare-earth elements present. Reference to domestic resources of monazite and their rare-earth oxide contents, described in the chapter on rare-earth metals, indicates the presence of a substantial domestic supply of yttrium in monazite.

Xenotime, found in small quantities with monazite, has been processed very little for its yttrium content, and, although the yttrium oxide content of the mineral is substantial, the yttrium resources estimates for this mineral are included with monazite. In addition, although the yttria content of bastnaesite is lower than the lowest noted for monazite—0.2 percent or lower—the large California bastnaesite deposit contains about 10,000 tons of yttrium oxide. The euxenite deposit in Idaho, formerly mined primarily for its columbium, tantalum, and uranium content, was estimated to contain 7,500 tons of the mineral with about 20 percent, or 1,500 tons, of yttrium oxide.

It is possible that nearly 30,000 tons of yttrium oxide is present in the various domestic ores. This conforms closely with estimates that the supply of yttrium from these sources is no more than 10 percent of the available cerium (*13*). Not included in these estimates are large quantities of yttrium in apatite contained in tailings from magnetic iron ore processing.

PRODUCTION, CONSUMPTION, AND TRADE

Practically all of the more recent production of yttrium metal and compounds for research purposes was sponsored by Government agencies, principally by the AEC. During the period 1957 through 1959 two organizations made about 15 tons of production-grade metal and sponge (*4*) and over 30 tons of yttrium fluoride was produced for use in the preparation of the metal (*3*). At times during this period total yttrium oxide production reached peaks of over 2 tons per month. Since then, however, yttrium production has dropped considerably and most of the current small demand has been for high-purity materials in electronics and in metallurgical research. Metal production since 1960 probably has not amounted to much more than 200 pounds; oxide production for 1962 and 1963 has averaged about 5 tons a year. Tariff rates on yttrium metal and alloys are included in those for processed rare-earth materials.

STRATEGIC CONSIDERATIONS

Despite the low yttrium content in bastnaesite, any conceivable emergency demand could be met by the processing of domestic bastnaesite and monazite or by the reactivation of additional monazite and the Northwest euxenite operations.

Yttrium is not on the Government list of strategic materials for stockpiling but is associated with rare-earth materials in various Government stockpiles. A considerable quantity of REO, and yttrium, will be in excess because of the new, lower objective of 3,000 short tons of REO for the strategic stockpile announced early in 1964. In addition, industrial stocks are large, and the AEC holds in inventory large quantities of yttrium metal, alloys, fluorides, and oxides. Well dispersed plants, now operating below capacity, easily could handle raw materials coming from amplified or reactivated mining operations.

PRICES

Monazite, prices of which are shown in the chapter on rare-earth metals, is the only yttrium-bearing ore or concentrate which is quoted on the open market. Sales contracts are written on large quantities, or purchases are directly negotiated between buyer and seller on small lots of ore or concentrate. No sales have been noted on any ores except monazite and bastnaesite since 1959, at which time contained yttrium brought from 50 cents to $1 per pound, depending on grade.

Recently, production chemical grades of yttrium oxalate and oxide of 70 to 85 percent purity sold for $18 and $36 in from 1- to 49-pound lots. In contrast, research quantities of anhydrous yttrium chloride and fluoride, from the same company, were $73 and $80 per pound package, respectively.

In 1963 one major producer raised prices substantially on its highest purity grades of yttrium oxide while another dropped prices on a number of grades. Nevertheless, prices on 99 percent to 99.9999 percent pure yttrium oxide ranged from $45 to $500 per pound in lots of 2 to 99 pounds. Low-oxygen yttrium metal ingots or lumps, of 99.9 percent purity, sold for $350 per pound in lots from 1 to 25 pounds; other yttrium metal of various purities, forms, and lot sizes, available from four companies, sold from $125 to $340 per pound. An 80 percent yttrium-magnesium alloy, in ingot or lump form, was $90 per pound in 1 to 25 pound lots; an yttrium misch metal was $38 per pound in 2 to 10 pound lots.

TAXES

With the exception of monazite, a 15-percent depletion allowance can be obtained on the gross incomes from the mining of domestic and foreign rare-earth and yttrium-bearing minerals. Monazite, because it contains thorium, is eligible for a 23-percent depletion allowance when it is mined domestically, and 15 percent, when it is mined from foreign deposits.

RESEARCH

Investigations on yttrium have always been included in research by the rare-earth industry and by other organizations and laboratories conducting studies on the processing, properties, and uses of the rare-earth elements. At the four rare-earth research conferences held in the United States from 1960 through 1964, yttrium phase studies were discussed, metal production and fabrication described, and geochemical abundance data presented.

Research has been sponsored by the AEC and the Department of Defense at university, industrial, and government laboratories. The separation of yttrium and the individual rare-earth elements by ion exchange at Iowa State College (now Iowa State University) and at Oak Ridge National Laboratory (ORNL) was sponsored by AEC. More recently experiments have been conducted at Ames Laboratory (Iowa State University) on the extrusion of seamless yttrium tubing from recrystallized billets (*12*). Geochemical abundance data have become available through programs financed by National Aeronautics and Space Administration (NASA). Research Chemicals, a division of Nuclear Corporation of America, conducted research on the properties and phase relationships of yttrium metal and alloys for the U.S. Air Force.

The Federal Bureau of Mines has conducted research on the extraction, production, refining, and properties of yttrium at its Albany (Oreg.) and Reno (Nev.) Metallurgy Research Centers.

OUTLOOK

Most of the yttrium raw material should be obtained as a byproduct of monazite and bastnaesite operations but, if demand should increase sharply, the outlook is promising for developing additional supplies from yttrium mineral deposits or from other mineral operations. Typical of this is the possible recovery of substantial quantities of yttrium and yttrium subgroup elements from apatite in Adirondack magnetic iron ore tailings. In addition, a substantial quantity of yttrium metal and compounds, remnants of experimental work on nuclear reactor materials used in such projects as the discontinued Aircraft Nuclear Propulsion (ANP) program, will probably be available to industry from the surplus inventory held by the AEC.

Most of the yttrium consumed is used in electronic equipment, with lesser quantities being used in alloys. Continually expanding usage in microwave devices such as yttrium-iron garnets will not require any additional sources of yttrium than those mentioned. However, newer potentially large requirements for yttrium and its compounds for alloy or ceramic applications may ultimately require the exploitation of or possible exploration for yttrium mineral deposits. To date, yttrium materials have been too expensive and too controversial to be considered seriously by industry for such large-scale uses as in nodularizing cast iron.

PROBLEMS

Similarities exist between the resource problems of yttrium and those of the rare-earth elements with which it is associated. The complex relationship between all these elements manifests itself in their production, separation, and marketing. Their association creates supply problems due to the accumulation of large quantities of certain less needed or unused rare-earth elements. This problem is not as acute with yttrium, principally because of its low content in the common rare-earth ore minerals. On the other hand, the supply of yttrium now in the possession of industry exceeds the demand. Furthermore, there are excess stocks of yttrium metal, alloys, compounds, and concentrates held by the AEC. As stated previously, it is almost certain that this total quantity will suffice for most of the current uses, even considering their expansion in the near future.

Much of the difficulty encountered in developing newer uses, such as that of yttrium nodular iron, stems from the high cost of the material needed. Lower cost material would become available if larger quantities were available. Conversely, only if there were a demand for much larger quantities of yttrium, for a reason such as the commercial production of yttrium-bearing alloys, will there be the need for exploring for yttrium-group rare-earth minerals or recovering these elements as byproducts from other current operations.

New exploration techniques or detection methods would be a boon to prospectors searching for yttrium and rare-earth elements. Collection of complete geochemical and mineralogical occurrence data would assist in evaluating byproduct and coproduct sources.

At this time, the problems of extraction and separation technology are not as critical as those of developing large-scale or newer uses. However, clean-cut separation of yttrium from certain rare-earth elements is difficult. Purification techniques also need improvement so that larger quantities of extremely pure yttrium would become available at lower cost for utilization research. Concurrently, extraordinary analytical methods are needed to test for minute quantities of impurities.

Some results of yttrium research and data accumulation are not yet available to the public. This is due largely to restrictions placed by both government and producers on the publication of certain information concerning potential fields of use.

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ZINC

By Harold J. Schroeder [1]

ZINC is a relatively soft, metallic element with a bluish-white color when freshly fractured. Although it has been used as a component of brass for 2,000 years, it was not until the middle of the 18th century that the metal was produced commercially in Europe. Thereafter new uses and increased demand for old uses multiplied the demand for zinc greatly. World smelter production now approximates 3.8 million tons annually, a quantity exceeded only by steel, aluminum, and copper production.

About 300 firms mine, smelt, import, or market zinc in the United States. Eleven firms operate 15 primary zinc smelters accounting for 98 percent of slab zinc output. Seven of the smelting companies operate mines which produced about 64 percent of domestic mine output.

For nearly all of the last 50 years the United States has led the world in producing and consuming zinc ores and metal. During 1925–53, U.S. mines produced one-third of world mine output, its smelters reduced 40 percent of all refined zinc, and its industries consumed 40 percent of world supply. In recent years world mine and smelter production have increased relative to that of the United States and in 1959–63 domestic mines and smelters produced but 13 and 26 percent of the world output, respectively. During 1963 the United States consumed 1.1 million tons of slab zinc, or about 29 percent of world consumption.

World War II marked the beginning of U.S. dependence on imports for an appreciable part of its needs. For many years the United States had been a net exporter of zinc, but beginning in 1940 and continuing thereafter greatly increased domestic requirements and domestic mine output below wartime levels necessitated importation of large tonnages of foreign metal, ores, and concentrates to augment supplies. Return to self-sufficiency is unlikely in the near future because large reserves of high-grade ores combined in some cases with lower labor cost permits foreign production at costs lower than can be attained for many domestic deposits. Average annual imports for 1959–63 of slab zinc or recoverable as slab zinc was 541,000 tons. Canada and Mexico, the second and fifth largest producers of mined zinc in recent years, are historically the chief sources of U.S. imports.

The major producers of zinc on a mine basis in order of output in 1963, were the United States, Canada, the U.S.S.R., Australia, Mexico, Japan, Peru, Poland, Italy, and the Congo (Leopoldville). The leading four countries furnished 47 percent of the 4.0 million tons of mine output in 1963. Estimated world smelter output in 1963 was 3.8 million tons of which 58 percent was produced by 5 countries—the United States, the U.S.S.R., Japan, Canada, and Belgium in ranked order.

World reserves of zinc in measured and indicated ore classifications are estimated to contain 85.0 million tons of zinc. Canada with 19.0 million tons has the largest reserve, followed by the United States with 12.2 million tons. The Western Hemisphere contains about 48 percent of the total reserve. Estimates of zinc in inferred ore are not available, but past experience indicates such quantities may be expected to exceed the sum of measured and indicated reserves.

The outlook for future zinc demand in the United States is for continued growth with little change in present use patterns. Requirements are expected to approximate 1.3 million tons annually by 1970 and 1.6 million tons by 1980. Domestic mine output will continue to be a substantial part of supply, and imports will probably increase providing that the import quota restrictions imposed in 1958 are relaxed. The 1.6 million tons of surplus zinc in the national stockpile is an additional potential supply source that must be taken into account.

[1] Commodity specialist.

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BACKGROUND

Zinc, as a component of brass, was used in China and Rome 2,000 years ago, long before it became known as an element. The first commercial metal production is credited to the Chinese in the 14th century A.D., but the events were poorly recorded. Zinc was smelted in Bristol, England about 1740, and the first continental European smelter was erected at Liege in 1807. As the demand for zinc increased, new ore sources and smelters were developed in Germany and Russia.

Commercial production of zinc in the United States began in 1860 when smelters were constructed at Friedensville, Pa., and La Salle, Ill. Thereafter, as demand increased, additional ore bodies and new smelting works were developed and by 1880, 13 smelters were producing about 23,000 tons of refined zinc annually. Statistics of smelter production show a strong, growing industry yielding 64,000 tons of zinc in 1890, 124,000 tons in 1900, and 256,000 tons in 1909 when the United States became established as the leading producer. The smelter growth rate of the United States was maintained during World War I when most continental European sources of refined zinc were unavailable to the Allies; by 1917 output was 686,000 tons, a quantity not exceeded until 1940. In 1943, the peak year of World War II, U.S. smelter output was 991,000 tons. Postwar demand for zinc remained high and an alltime output of 1,058,000 tons was attained in 1957. After a slump to 828,000 tons the following year there was a slow upward trend to 953,000 tons by 1963.

During the period of rapid growth, the industry was stimulated by tremendous industrial expansion, the discovery of numerous ore bodies, and the development of many new techniques in mining, milling, and smelting. These new techniques included high-speed drilling equipment, improved explosives, power loading devices, electrically powered pumps, fans, and haulage motors, and rubber-tired ore loading and transporting equipment powered by internal combustion engines. Developments in the flotation process about 1918 permitted economic use of large reserves of complex and fine grained ores, formerly marginal because of high metallurgical losses and treatment charges. In smelting, the introduction of electrolytic zinc reduction plants about 1915 and later The New Jersey Zinc Co.'s continuous distillation process and rectification column provided new methods of producing high-purity zinc suitable to a wider range of uses than grades formerly produced.

Demand for zinc in the United States has outstripped domestic supply, and since 1940 the Nation has become a large importer of zinc ore and metal.

Acquisition of 1.6 million tons of zinc metal by the U.S. Government between 1946 and 1960 for a national stockpile has been a significant factor in the zinc industry. The stockpile was substantially completed early in 1958 and in October 1958 import quotas were imposed to curtail further build up of industrial stocks and alleviate injury to the domestic industry.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Zinc is one of the four metals produced and used in greatest quantity by industrialized nations. In the United States it ranked fourth in tonnage of metals produced and consumed in 1963, following iron, aluminum, and copper. The United States has been the world's foremost producer of zinc in ore and refined form for 50 years except for 1958 when Canada surpassed the United States in mine output. Over the 5-year period 1959–63 the United States produced 13 and 26 percent of world mine and smelter production, respectively. Other leading producers of zinc ore in 1963, ranked in order of output, were Canada, the U.S.S.R., Australia, Mexico, Japan, Peru, Poland, Italy, and the Congo (Leopoldville). Other principal smelting countries were the U.S.S.R., Japan, Canada, Belgium, Australia, Poland, France, and West Germany. The smelter output of the five leading nations including the United States was about 58 percent of the world total; that of the Western Hemisphere about 34 percent.

The U.S. zinc industry is made up of about 300 units which mine domestic ores, import foreign ores, purchase scrap, or smelt or otherwise process these raw materials into slab zinc, zinc pigments, dust, alloys, or other zinc products.

Eleven firms operate 15 primary zinc smelters. These firms listed in descending order of slab zinc output for the period 1961–63 are St. Joseph Lead Co., New Jersey Zinc Co., American Smelting and Refining Co., The Anaconda Company, American Zinc, Lead and Smelting Co., The Bunker Hill Co., Blackwell Zinc Co., The Eagle-Picher Co., The National Zinc Co., Matthiessen & Hegeler Zinc Co., and Athletic Mining & Smelting Co. The leading four companies accounted for 57 percent of output and the total for all primary producers was about 98 percent. Ten companies with secondary smelters produced the remaining 2 percent of slab zinc. Smelter data are shown in table 1.

TABLE 1.—*U.S. primary and secondary zinc plants, their location and capacity for slab zinc in 1963*

Type of plant and company	Plant location	Slab zinc capacity (short tons)
Primary plants:		
Electrolytic:		
American Smelting and Refining Company	Corpus Christi, Tex	507,500
American Zinc Co. of Illinois	Monsanto, Ill	
The Anaconda Company	Anaconda, Mont	
Do	Great Falls, Mont	
The Bunker Hill Co	Kellogg, Idaho	
Horizontal-retort:		718,800
American Smelting and Refining Company	Amarillo, Tex	
American Zinc Co. of Illinois	Dumas, Tex	
Athletic Mining & Smelting Co	Fort Smith, Ark.[1]	
Blackwell Zinc Co., Division of American Metal Climax, Inc.	Blackwell, Okla	
The Eagle-Picher Co	Henryetta, Okla	
Matthiessen & Hegeler Zinc Co	LaSalle, Ill [2]	
National Zinc Co	Bartlesville, Okla	
Vertical-retort:		
Matthiessen & Hegeler Zinc Co	Meadowbrook, W. Va	
The New Jersey Zinc Co	Depue, Ill	
Do	Palmerton, Pa	
St. Joseph Lead Co	Herculaneum, Mo [3]	
Do	Josephtown, Pa	
Secondary plants:		63,500
American Smelting and Refining Company	Beckemeyer, Ill	
Do	Sand Springs, Okla	
Do	Trenton, N.J	
American Zinc Co. of Illinois	Hillsboro, Ill	
Apex Smelting Co	Chicago, Ill	
Arco Die Cast Metals Co	Detroit, Mich	
W. J. Bullock, Inc	Fairfield, Ala	
General Smelting Co	Bristol, Pa	
Gulf Reduction Co	Houston, Tex	
H. Kramer Co	El Segundo, Calif	
Pacific Smelting Co	Torrance, Calif	
Sandoval Zinc Co	Sandoval, Ill	
Superior Zinc Corp	Bristol, Pa	
Wheeling Steel Corp	Martins Ferry, Ohio	

[1] Plant closed November 1963.
[2] Plant closed July 1, 1961.
[3] Electrothermic slag-fuming unit, yielding a slab zinc product.

Seven of the smelting companies also own and operate zinc mines in the United States. These seven in 1961 accounted for 64 percent of zinc mine output and the four largest accounted for 56 percent. Listed in descending order of production the companies were New Jersey Zinc Co., St. Joseph Lead Co., American Zinc, Lead and Smelting Co., The Bunker Hill Co., The Eagle-Picher Co., American Smelting and Refining Co., and The Anaconda Company.

Companies reporting mine production of zinc in the same year and not integrated with smelters numbered about 240. The leading 15 companies accounted for 31 percent of domestic mine output. The next 28 companies accounted for 4 percent and the remaining 197 for only 1 percent. The leading 15 listed in descending order of output are United States Smelting, Refining and Mining Co.; Tri-State Zinc, Inc.; Shattuck Denn Mining Corp.; United States Steel Corp., Tennessee Coal & Iron Division; Pend Oreille Mines and Metals Co.; Idarado Mining Co.; Hydrometals, Inc. (American Peru Mining Co.); Tennessee Copper Co.; United Park City Mines Co.; Cyprus Mines Corp.; Ozark-Mahoning Co.; Minerva Co.; McFarland & Hullinger Co.; New Park Mining Co.; and Camp Bird Colorado, Inc.

Some of the companies prominent in the U.S. zinc mining or smelting industry have substantial investments or control of important zinc mines in Canada, Mexico, Argentina, Peru, Australia, South-West Africa, and Morocco. Among these are American Metals Climax Co., American Smelting and Refining Co., Pend Oreille Mines and Metals Co., and St. Joseph Lead Co. Other important foreign zinc operations controlled or substantially owned by American corporations are Peruvian mines and smelters by Cerro de Pasco, Mexican Mines by the Fresnillo Co. and diversified investments by Newmont Mining Corp.

There are many large and small mines and more than 60 smelters abroad which produce about two-thirds of the world's zinc. Major foreign mining and smelting companies include Consolidated Mining and Smelting Co. and Hudson Bay Mining and Smelting Co. in Canada; Cia Royale Asturienne De Mines, Societe des Mines et Fonderies de Zinc de la Vieille-Montagne, and Societe Miniere et Metallurgique de Penarroya in North Africa, Spain, Belgium, or France; Union Miniere du Haut Katanga and its subsidiary Metalkat with mines and smelter in the Congo (Leopoldville); Rhodesian Broken Hill Development Co., Ltd., with mine and smelter in Northern Rhodesia; Rio Tinto-Zinc Corp. owner of the Zinc Corp., Ltd. and other interests in the Broken Hill district of New South Wales, Australia, as well as zinc and other smelters in the United Kingdom; E Z Co. of Australia; Mitsui Mining & Smelting Co., Ltd., Mitsubishi Metal Mining Co., Ltd., and Toho Zinc Co. in Japan; as well as numerous others in the same countries as well as elsewhere.

U.S. mine production of 529,000 tons of zinc in 1963 came from approximately 250 mines in 22 States. The 25 leading zinc-producing mines yielded 81 percent of domestic output and the leading 4 mines supplied 25 percent of the total. States east of the Mississippi River produced 51 percent of the total output; Western States, 46 percent; and West Central States, 3 percent.

Concentration mills are at all the principal mines. Some operate as customs mills to process ores from mines without mills.

Zinc is smelted and refined at 17 primary and 11 secondary reduction plants in 12 States. The same plants also produce zinc oxide, zinc dust, zinc-base alloys or zinc pigments and salts.

Although it is desirable for a smelter to be near its source of raw material, the governing factors in location of a smelter are availability of skilled labor, fuel, and power, and nearness to markets for sulfuric acid and refined zinc (*5*).[2] Only the Anaconda, Mont., Kellogg, Idaho, and Palmerton, Pa. smelters are situated within 30 miles of any zinc mine and both Kellogg and Palmerton rely on ores shipped many hundreds of miles for capacity operation. The location of the retort plants in Illinois, Oklahoma, and Texas were originally chosen because the site offered natural gas or coal and possibly retort clays also.

DEFINITIONS OF TERMS, GRADES, AND SPECIFICATIONS (*4*)

Zinc is a bluish-white metal with atomic weight of 65.38. Characteristic properties are specific gravity of 7.13 grams per cm at 20° C, melting point of 419.5° C, and boiling point of 906° C. The properties of being chemically active and alloying readily with other metals is utilized industrially in a large number of zinc containing alloys and compounds. The relatively high position of zinc in the electromotive series largely accounts for the extensive use of the metal to protect iron and steel products against corrosion. Commercial zinc cast in various smelter shapes and sizes is termed *slab* zinc in the United States; the older term *spelter* is now rarely used in this country.

Slab zinc is produced in six standard grades which range from about 98.3 to more than 99.99 percent zinc.

The specifications (ASTM designation: B 6–61) for primary slab zinc provide that the zinc be made from ore or other material by distillation or electrolysis, and not by "sweating" or remelting of scrap. The grades and maximum impurities are shown in table 2.

TABLE 2.—*Grades of slab zinc*

Name	Maximum, percent [1]				Minimum percent zinc [2]
	Lead	Iron	Cadmium	Total	
Special High Grade	0.006	0.005	0.004	0.010	99.99
High Grade	.07	.02	.07	.10	99.90
Intermediate	.20	.03	.50	.50	99.50
Brass Special	.60	.03	.50	1.0	99.00
Selected	.80	.04	.75	1.25	98.75
Prime Western	1.60	.08			98.3

[1] ASTM Standards, 1961, part 2, p. 636.
[2] Difference, by deduction of listed allowable impurities.
NOTE.—Analysis shall not regularly be made for tin but when used for die castings, if found, by the purchaser, tin shall not exceed 0.003 percent. Greater amounts may constitute cause for rejection.
Where it is specified by the purchaser at the time of purchase that the special high-grade zinc is to be used for the manufacture of zinc-base, die-casting alloy ingot, the maximum permissible tin content shall be 0.002 percent and the maximum permissible lead content shall be 0.005 percent.
Analysis shall not regularly be made for aluminum. When used for the manufacture of rolled zinc or brass, aluminum, if found by the purchaser, shall not exceed 0.005 percent. Greater amounts may constitute cause for rejection.

The refined zinc is cast into slabs typically weighing 55 pounds, each of which is identified as to grade and producer by the registered brand name cast into the metal. The slab metal is commonly loaded and strapped onto pallets designed for fork-lift handling. Such zinc pallet loads weigh 2,000 to 2,500 pounds each.

Zinc produced from newly mined ores is termed primary or virgin zinc. When zinc is produced from scrap or residues, it is termed secondary *redistilled* or *remelt* zinc dependent upon the process utilized for recovery. Primary zinc is referred to as *electrolytic* or *distilled* zinc according to the reduction process used. Refined zinc refers to an upgraded distilled zinc sometimes accomplished by repeating the original process when it is designated as redistilled zinc. All of the above terms are mainly descriptive of source of material or process of produc-

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

tion and only generally denotes grade, thus certain brands classed as refined zinc are lower in purity than others simply classed as distilled zinc.

Zinc die casting alloys are any of several zinc-base alloys in which aluminum and copper are the principal alloying elements. The most widely used of these alloys have compositions described by ASTM Specification B 86, Alloys AG40A and AC41A. These alloys contain from 3.5 to 4.3 percent aluminum and from 0.03 to 0.08 percent magnesium. The aluminum imparts desirable mechanical properties to the alloy, and the magnesium counteracts subsurface corrosion caused by certain impurities. Alloy AC41A contains 0.75 to 1.25 percent copper and AG40A up to 0.25 percent copper to improve tensile strength, hardness, and other physical properties.

Copper-base alloys in which zinc is the principal alloying element and ranges from about 5 to 40 percent by weight is called *brass*. Some bronzes whose principal alloying materials are copper and tin also contain up to 4.5 percent zinc.

Zinc burns in air with a brilliant green-blue light to form the white powdery *zinc oxide* used widely in pigments and rubber. Table 3 presents ASTM Specifications (D–79–44) for American and French process zinc oxide.

Zinc is available as a semimanufactured product in the form of dust. Although standard specifications have not been adopted by the industry, chemical purity and particle sizes are closely controlled to particular customer requirements. Commercial zinc dust produced ranges from 95 to 99.8 percent zinc with the balance principally oxidized zinc and also as impurities of lead and iron. A representative particle size gradation would be 100 percent minus 100-mesh and 25 percent minus 325-mesh although some specifications call for more than 97 percent passing a 325-mesh screen.

TABLE 3.—*ASTM specifications for American and French process zinc oxide*

	American process	French process
Zinc oxide, minimum percent	98.0	99.0
Sulfur, maximum percent	.2	.1
Moisture and other volatiles, do	.5	.5
Total impurities, do	2.0	1.0
Retained on 325-mesh (44-micron) sieve, do	1.0	1.0

TECHNOLOGY (*1, 9*)

Geology

Numerous minerals contain zinc but the principal ore mineral is the sulfide, sphalerite, sometimes called "blende". An exception is the unique and very important deposit found at Ogdensburg, N.J. composed of zincite (ZnO), willemite (Zn_2SiO_4), and franklinite (Fe,Zn,Mn)O. $(Fe,Mn)_2O_3$. Zinc sulfide oxidizes readily to the common minerals smithsonite ($ZnCO_3$) and hemimorphite ($H_2Zn_2SiO_5$). These oxidized zinc ores used to be mined extensively but are now treated only a few places in the world because of poor metallurgical recoveries and economic considerations.

Sphalerite is commonly associated with lead and iron sulfides and to a lesser degree with copper sulfides and gold and silver minerals. The zinc ores of the Mississippi Valley and Eastern United States are characterized by simple mineralization, the zinc being present with relatively minor quantities of lead and little or no copper, gold, and silver. Most sphalerite has associated cadmium as a coating or solid solution in quantities from traces to 2 percent. Other metallic elements commonly associated with sphalerite in small quantities include germanium, gallium, indium, and thallium.

Most economic deposits of zinc are cavity fillings, replacements, or combinations believed to have been deposited by mineral-bearing solutions of magmatic origin. Cavity fillings include the fissure veins in San Juan and San Miguel Counties, Colo., the breccia ores in the Jefferson City-Mascot area of Tennessee and the Austinville area of Virginia, and the cave and fracture fillings ("pitches and flats") of the upper Mississippi Valley area. Replacements also play a part in these same deposits. The extensive replacement deposits in limestones are typified by deposits at Leadville, Colo.; Bingham and Tintic, Utah; eastern Tennessee; and Metaline area of Washington. Fissure fillings with wall rock replacement form the lode deposits of Butte, Mont.; the Coeur d'Alene district, Idaho; and Park City, Utah.

Important foreign mines based on fissure veins and wall rock replacement include the Cerro de Pasco in Peru; the Fresnillo, San Francisco del Oro, Parral, Santa Barbara, and Pachuca in Mexico. The ore bodies at the Sullivan and Flin Flon mines in Canada and the Mt. Isa and Broken Hill mines in Australia are massive sulfide replacements in metamorphosed sediments or igneous rocks.

Grades of ore mined vary widely throughout the world depending on the natural resource, technologic, and economic factors. A 1960 study of ores mined and milled in the United States showed that for 25 operations classed as lead-zinc ores the average grade was 3.45 percent zinc and 0.95 percent lead; for 29 operations classed as copper-lead-zinc ores the average grade was 3.26 percent zinc, 2.51 percent lead, 0.50 percent copper, 3.45 ounces of silver per ton, and 0.017

ounces of gold per ton. Variations between mining districts are great as shown by table 4.

TABLE 4.—*Selected examples of approximate ore grades*

District	Zinc, percent	Lead, percent	Silver, ounces per ton
Coeur d'Alene	4.3	5.8	4.0
St. Lawrence County, N.Y.	9.0	.15	
Upper Mississippi Valley	3–7	0.5–1.0	
Kansas and Oklahoma [1] [2]	2.0	.3	
East Tennessee	2–6		

[1] Portion of Tri-State district.
[2] Grades in earlier years were commonly about 10 percent of combined lead and zinc.

For comparison some of the ore grades of important zinc producing mines in Canada are the Sullivan mine, about 10 percent combined lead and zinc plus values in gold and silver; the Flin Flon mine, 4.7 percent zinc and 2.25 percent copper; Mattagami Lake district mines, 12.5 percent zinc, 0.7 percent copper, and 1.3 ounces of silver per ton; and the Geco mine, 4.6 percent zinc, 2.1 percent copper, and 2.3 ounces of silver per ton.

The Fresnillo and Naica mines in Mexico average about 5.0 percent zinc, 5.3 percent lead, and 5.4 ounces of silver per ton. In Australia mines in the Broken Hill district average about 11.2 percent zinc, 12.6 percent lead, and 5.0 ounces of silver per ton. The Mount Isa mine in Queensland, Australia has reserves estimated to contain 7.8 percent lead, 5.5 percent zinc, and 5.6 ounces of silver per ton.

Prospecting and Exploration

During the last half of the 19th century when the U.S. demand for zinc ores began, reserves were primarily developed coincident with the exploration and mining of lead, copper, gold, and silver ores.

Most of the important zinc producing mines of the United States except those of eastern Tennessee, St. Lawrence County, N.Y., Sussex County, N.J., and the Picher portion of the Tri-State district began as lead or lead-silver mines discovered on the basis of outcrops. As the easily discovered ore bodies were depleted, prospecting techniques were developed involving geologic mapping of rock units and structures to evaluate the structural conditions, mineralizing solutions, reactive gangue, and other control factors.

In the period since World War II geophysics and geochemistry have been used increasingly in mineral exploration. Geophysical exploration is a highly specialized field of engineering requiring a thorough knowledge of physics, mathematics, geology, and their related field application to make careful measurements of physical properties such as magnetic susceptibility, density, electrical conductivity, and radio-activity. Airborne magnetic surveys in southeast Missouri in 1948 and airborne electromagnetic measurements in New Brunswick and Ontario in 1953 were instrumental in the discovery of large reserves of base metals, including zinc. Geochemistry has been widely used in Tennessee, Virginia, and elsewhere to determine favorable areas for drilling on the basis of anomalous quantities of zinc in the soil or vegetation (*6*).

The final step in the prospecting and the most important part of the exploration phase is to obtain actual samples and some direct knowledge of the deposit. Where the deposit outcrops at or near the surface, trenches or pits provide a simple means of exposing the mineralized zones. Boreholes, shafts, and adits are used to explore deeper portions of a mineral deposit. Drilling is the most universal method employed to obtain samples. Churn, rotary, and percussion are drilling methods used. Diamond drilling, one of the rotary methods, has attained widespread use since it permits orientation of the hole in any direction, penetrates to depths of several thousand feet, and provides a solid core of the mineral formations for study and analysis. Descriptions of drill equipment and their operation is not included here since this information is readily available in general texts on mining.

The pattern, spacing, and sampling of openings is designed to obtain adequate knowledge of the deposit to determine reserve figures and for initial planning of subsequent mining operations. Preliminary determination of amenability of the ore to beneficiation is also usually a part of the exploration work.

Mining

Most zinc is mined using underground mining methods, principally classed as open, shrinkage, cut-and-fill, or square set stoping methods. A few mines, particularly in their early stages of operation, mine zinc by open pit methods. Open stopes with pillars (breast stopes) are employed exclusively in mining the near-flat lying ores of the Metaline, Tri-State, Upper Mississippi Valley, Tennessee, and Virginia mining districts. The rock structure overlying the ore deposit being mined is supported by the walls of the stope and such pillars as are necessary to assure safe working conditions. If the width of the ore body is such that the roof-span will stand without pillar supports, the entire ore body may be extracted. Ore bodies having large horizontal extent require a system of pillars to support the roof, with the position and size of

the pillars dependent on mass rock mechanics of the pillars, walls, roof, and floor. Optimum roof conditions compatible with allowable costs often require that some ore be left as part of the roof, or that waste-rock be shot down. As mining progresses to new areas, some pillars may be removed and others reduced in size. Despite such pillar recovery ore remaining as ground support commonly ranges up to 30 percent of the ore shoot, and may average about 15 percent.

Owing to the shape, size, and position relative to the surface and the frequently fractured, altered nature of the ore and surrounding wall rocks, most stopes in mines in the Western States require artificial support. The mining method employed is usually some form of filled stope such as cut-and-fill, filled square set, or by shrinkage stopes which are subsequently filled.

Top slicing and caving methods are little used as primary stoping methods, but find some use in combined methods in which stoping is by square-setting or shrinkage, and the stope pillars are mined by top slicing or caving.

Mechanization during the past 50 years has progressively lessened the hand labor of mining and led to greatly increased output per man-shift. The rate of ore breakage has been increased by the introduction of light-weight rock drills using drill steel with detachable alloy or carbide bits. Hand loading in drifts, crosscuts, and shafts has been replaced by loading machines of various types, and in many instances chute loading has been replaced by machine loading from drawpoints in the stope floor. Increasing mining depth has brought many additional problems. These include the necessity of supporting increasingly heavy ground or devising methods adapted to it. Added depth has also increased the burden of pumping, ventilating, hoisting, and securing mine fill.

The large, single-level, open stopes of the Tri-State, Tennessee, and Metaline districts have adopted "trackless" mining in which jumbos, power loading equipment, and haulage units are mounted on crawler-type tread or pneumatic-tire vehicles. The working speed and facility of movement from work face to work face gives greater capacity with lower mining costs which in some cases permit mining ore containing as little as 2 percent zinc.

Milling

Milling consists of separating the desirable mineral constituents in an ore from the unwanted impurities (gangue) by various mechanical processes. Terms used somewhat interchangeably for milling include concentration, ore beneficiation, ore dressing, and mineral dressing. Liberation of the minerals by crushing and grinding is followed by subjecting the discrete particles to forces of gravity, magnetism, or solid-liquid-gas surface phenomenon relations (flotation process). The upgraded mineral products are termed concentrates, the rejects are called tailings, and poorly separated intermediate products destined for additional milling are termed middlings.

Compelling reasons for milling an ore include large savings in shipment costs by not transporting worthless waste material long distances from mine to smelter; efficient utilization of fuel and facilities in the metal reduction or other treatment process; and improved metallurgical results when using a relatively clean, high-grade concentrate.

The particular combination of ore-dressing equipment used differs with the quantities and kinds of ore minerals present, their values, the character of the gangue minerals, and the mineral particle sizes. Simple ores, such as coarsely disseminated zinc or zinc-lead minerals occurring with a low specific gravity gangue, are readily treated in heavy-medium cones, jigs, and tables after being crushed and rolled in closed circuit with vibrating or trommel screens and classifiers to give properly sized feed. Selective or differential flotation to the slime products or of a reground middling product completes the flowsheet. Ores of this kind are common in the mines of the Mississippi Valley and Eastern United States. In some instances the ores are concentrated wholly by flotation.

The more complex sulfide ores, such as those in the Western United States, consist of disseminated mixtures of fine-grained lead and zinc sulfide, usually accompanied by pyrite, some copper sulfides, and some gold and silver in a country rock, quartz, or quartz-calcite gangue. Concentration of such ores may be complicated by partial oxidation of the sulfides and the presence of high-density gangue minerals such as barite, siderite, or rhodochrosite. Such complex ores are crushed and fine-ground in closed circuit to a size at which the ore minerals are freed from the gangue. The ore is then selectively floated to yield lead, zinc, and copper or copper-pyrite concentrates; middling products are reground and recycled to complete the recovery.

The low capital and operating costs of the heavy-medium plant make it very effective for producing a rough zinc concentrate and eliminating a large fraction of the gangue minerals in simple ores. Such units, using ferrosilicon as the heavy medium, have been used extensively in eastern Tennessee and the Tri-State area to treat ore.

A 1960 milling study in the United States showed that for 25 operations classed as treating lead-zinc ores, 14 used flotation, 11 used

gravity plus flotation, and 14 used flotation alone to produce zinc concentrates. The combined operating results showed production of zinc concentrate averaging 59.85 percent zinc and achieving a 92 percent recovery of the zinc in the ore. For 29 operations classed as treating copper-lead-zinc ore, the zinc concentrate averaged 53.43 percent zinc and recovered 86 percent of the zinc. An additional 6 and 1 percent of the zinc was recovered with the lead and copper concentrates, respectively.

In recent years no oxidized ores have been treated in the United States. Data available for a foreign plant operating on oxidized ore shows the following results: Feed—5.0 percent zinc, 2.5 percent lead; zinc concentrate—39.5 percent zinc, 2.5 percent lead; lead concentrate—68.7 percent lead, 3.9 percent zinc; and recovery of zinc—54.7 percent.

Smelting and Refining (*1, 7*)

The reduction of zinc ores and concentrates to zinc is accomplished by electrolytic deposition from a solution (electrowinning or hydrometallurgy of zinc) or by distillation in retorts or furnaces. For either method the zinc concentrate is roasted to eliminate most of the sulfur and for conversion to impure zinc oxide called roasted concentrates or "calcines".

At electrolytic zinc plants the roasted zinc concentrate is leached with dilute sulfuric acid to form a zinc sulfate solution. The pregnant solution is then purified to remove contained copper, cadmium, cobalt, iron, etc., and piped to electrolytic cells, where the zinc is electrodeposited on aluminum cathodes. This zinc is either Special High Grade or High Grade. At intervals the cathodes are lifted from the tanks and stripped of the zinc, which is then melted in a furnace and cast into slab form. The electrolysis of the solution regenerates sulfuric acid, which is used in a succeeding cycle of leaching. Inasmuch as zinc concentrates shipped to electrolytic plants commonly contain lead, gold, and silver, the leach and electrolytic tank residues become enriched in these metals by the extraction of the zinc, and are usually shipped to a lead smelter. There the lead, gold, and silver content is recovered in lead bullion. Zinc reports with the lead furnace slag and is subsequently removed as an impure oxide by a fuming operation. The zinc fume, after de-leading and densifying in a kiln, forms a suitable feed for return to a zinc reduction plant.

Distillation retort plants are classified as batch horizontal retorts, continuous vertical retorts externally heated by fuel, and continuous vertical retorts heated electrothermally. All employ coal or coke as a reducing agent, quantities required range from about 0.5 to 0.8 tons per ton of slab zinc output. The zinc vapor and carbon monoxide from the retorts pass into condensers of various types where the zinc is collected as liquid metal ready for casting into slab form. Zinc produced by distillation are normally the lower commercial grades but may be upgraded by refining to reduce the quantities of the common impurities of lead, cadmium, and iron; also the lesser impurities such as copper, tin, and arsenic. Simple liquation removes lead down to the maximum solubility in zinc at its freezing temperature (1.2 percent lead) and also removes iron to a limited degree to produce a product conforming to the specifications for Prime Western grade zinc. Refining by redistillation is accomplished by vertical fractionating columns which separates the impurities contained in the feed zinc and can produce zinc of 99.995 plus purity.

The residues from distillation are shipped to a lead smelter for further processing when they contain economic quantities of lead, gold, or silver or are processed in a Waelz kiln when economic quantities of zinc with or without lead remain. The Waelzing operation consists of charging a mixture of residues and 10 to 15 percent coal or coke to a large oil-or-gas-fired rotary (Waelz) furnace. The high temperature (1,100° to 1,150° C) in combination with the carbon of the fuel causes volatilization of the lead and zinc which are collected as a fume product in a Cottrell precipitator or bag-house.

The blast furnace process of producing zinc, also known as the Imperial vertical-type smelter process, was introduced commercially in 1950 by Imperial Smelting Corp., Ltd., Avonmouth, England. Installations have been completed or are being built in England, France, Australia, Northern Rhodesia, and Canada. The normal blast furnace practice of burning carbonaceous matter in intimate association with the ore to be reduced is followed. However, as in other zinc distillation processes, the zinc is released as a vapor and must be condensed. An important advantage to the process is the ability to treat a mixed zinc-lead concentrate and recover both metals as well as any gold or silver present with no extra coke consumption and little extra labor. Metal produced by the blast furnace conforms to Prime Western grade, containing about 1.2 percent lead and 0.02 percent iron.

High-purity zinc for specialized uses has been made by zone refining. Zone refining is a process in which a short molten zone moves slowly but repeatedly through a bar of the material to be refined, redistributing the solutes or impurities through the mechanism of fractional crystallization as the molten zone travels from one end to the other. The molten zone contains a

melting liquid-solid interface and a freezing liquid-solid interface. At the melting interface all solid materials become mobile. At the freezing interface, the concentration of each impurity differs from that in the liquid phase. If the impurity is one which lowers the melting point of the zinc, it concentrates in the liquid phase and moves with it. If the impurity is one which raises the melting point of zinc, it tends to concentrate in free zinc solid and the liquid becomes depleted in that impurity. Experimental work by the Consolidated Mining & Smelting Co. of Canada, Ltd. at Trail, British Columbia, has produced zinc with lead and cadmium contents of but one part per million each. Thallium and bismuth also can be effectively removed by zone refining.

Metallurgical recoveries at zinc-reduction plants range from 89 to 97.5 percent, the range in recovery being governed by the nature of the smelter feed, the treatment process, and the economics of recovery.

USES

A large part of the world's zinc supply is used for protective coatings on steel and iron, principally by the hot-dip galvanizing process; zinc-base alloys for die-cast products; alloying constituent of brass; production of zinc oxide; and wrought or rolled zinc products.

Domestic consumption of zinc has normally been in the order listed when the comparison includes the direct production of zinc oxide from ore and scrap zinc. However, zinc consumed in diecasting has in some years exceeded the use for galvanizing and these two together account for approximately 65 percent of the total consumption of zinc from slab, direct consumption of ores, and zinc scrap.

TABLE 5.—*Slab zinc use pattern*

Slab zinc used in	Percent of total		
	1961	1962	1963
Zinc-base alloy for die castings	36	40	42
Galvanizing of sheet and strip	23	21	22
Galvanizing tubes and pipe	6	5	5
Galvanizing wire and wire rope	4	4	4
Rolled zinc	4	4	4
Sheet, strip, and plate	7	6	5
Rod and wire	4	4	4
Zinc oxide	2	2	1
Other	14	14	13
Total	100	100	100

The widespread use of zinc as a protective coating on iron and steel products is due mainly to (1) excellent resistance of zinc to normal weathering processes, (2) sacrificial nature of the zinc relative to iron (galvanic action), thus affording some protection to the iron exposed by cuts and scratches in the coating, and (3) economy of application.

Principal classes of material galvanized are sheet and strip, tubes and pipe, wire and wire rope, structural shapes, and a multitude of hardware fittings. Galvanized products are used in large quantities by the construction, agriculture, appliance manufacturing, and automotive industries. Specific applications of galvanized iron and steel products number in the thousands and include such well known articles as roofing and siding sheets, wire and wire products, water tanks, pipe, pails and cans, nails, screws, bolts, and hinges.

Most of the galvanizing is accomplished by immersion of the iron or steel article in molten zinc, a process known as hot-dip galvanizing. Much of the hot-dip galvanizing is now accomplished on high-speed continuous galvanizing lines, a process which gives improved and uniform zinc adherence and ductility as well as economical production. Electro-deposited zinc coatings are also used as this method of coating provides a product with properties that are particularly useful for sign work, lighting fixtures, cabinet applications, wire, and small or intricately shaped articles. Coatings are also applied by spraying, sherardizing, and painting.

Cathodic protection of underground and underwater structures, such as pipelines, storage tanks, ships' hulls, and steel piers, also depends on galvanic protection. Corrosion of steel is caused by the passage of an electric current from the steel to the surrounding soil or liquid. Zinc anodes bonded to the steel structure generate a countercurrent which stops the corrosive outflow of current and establishes a slight flow to the steel with accompanying long-term controlled corrosion of the zinc anode. Cathodic protection at 100 Naval shore installations between 1958 and 1968 is expected to reduce maintenance costs by $40 million, at a total cost of less than $500,000.

Zinc-base alloys for diecasting purposes has in recent years used approximately 40 percent of domestic slab zinc and 85 percent of Special High Grade zinc consumption. In the diecasting processes, castings are produced in quantity by forcing molten alloy into steel dies at temperatures up to 900° F and at pressures up to 2,500 pounds per square inch. Diecasting permits production of intricate parts within close limits of accuracy and yields extremely smooth surfaces that are easily plated with nickel-chrome finishes. Automobile hardware such as door handles, window cranks, horn rings, instrument panel parts, hood ornaments, and radiator grilles as well as fuel pumps, carburetors, parts for windshield wiper motors, heaters, and hydraulic brakes are commonly zinc diecastings. Zinc diecastings are also used

in electrical appliances, business machines, tools, building hardware, toys, and novelties. Another use of zinc-base alloys is to make forming, stretching, and drawing dies used by the aircraft and automobile industries in forming metal shapes from aluminum and low-carbon and stainless steels.

Zinc in brass ranges from 3 to 45 percent with the average brass containing about 30 percent zinc. Red brass pipe, 15 percent zinc, is widely used for water and other piping. Brass finds extensive use in the automobile industry for radiator cores and lamp reflectors. Other important uses include lamp fixtures, brass screws, bolts, locks and hinges, watch and clock parts, cartridge cases, and numerous parts for the radio, television, telephone, and telegraph industries.

Zinc oxide which is used in rubber, paints, ceramics, cosmetics, pharmaceuticals, textiles, and floor coverings requires about 20,000 tons of slab zinc, 90,000 tons of zinc in ore, and 25,000 tons of zinc in scrap. All rubber, natural and synthetic, contains an average of about 5 percent zinc oxide, natural rubbers more, synthetics less. Heavy duty tires use larger quantities because zinc oxide not only aids the curing process but reduces heat generation, dissipates heat rapidly, and adds reinforcement to the rubber bond (*2*).

Other important quantities of zinc are consumed as rolled zinc which is used in the popular battery dry cells, as extruded cans for radio condensers and tube shields, and to make weather stripping, photoengraving plates, and anodes to protect hot water tanks, boilers, ship hulls, and pipelines. In Europe, rolled zinc is widely used as a long-lived roofing material. Smaller, but still important, quantities of zinc are consumed as zinc dust (chiefly from scrap), in the manufacture of lithopone, zinc chloride, zinc ammonium chloride, zinc sulfate, zinc chromate, other chemicals, and light-metal alloys, and in the desilverizing of lead.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

The sources of zinc production, classified according to types of ore in 1963 were 44.7 percent from zinc ores; 43.6 percent from lead-zinc ores; 0.4 percent from lead ore; 6.0 percent from copper-lead, copper-zinc, and copper-lead-zinc ores; and 5.3 percent from all other classifications. These sources include ores with substantial gold and silver output. Manganese is a coproduct of zinc-lead manganese-silver ores at Butte, Mont. and zinc-manganese ores at Ogdensburg, N.J. In the Tri-State area tailings (chats), which are mostly flint and chert, are sold for railway ballast, roadstone, concrete aggregate, roofing granules, and sand for sand blasting. The Tennessee, Virginia, and upper Mississippi Valley product is limestone or dolomite which is almost all sold for use as agricultural limestone or as crushed stone.

In addition, the zinc smelters produced 862,000 tons of byproduct sulfuric acid from zinc concentrates in 1963. The smelters also recovered on the order of 9 pounds of cadmium for each ton of slab zinc produced from zinc concentrates. In addition smaller quantities of germanium, thallium, indium, and gallium were recovered from flue dusts and residues of zinc smelting operations.

Byproduct antimony, bismuth, and tellurium occur with the lead minerals in many of the zinc-lead ores from the Western States.

ALTERNATE MATERIALS

For galvanizing iron and steel products, one of the major uses of zinc, there is no adequate substitute. Ceramic and plastic coatings are now employed in a narrow field that may gain in future importance. Cadmium is used for electroplating, but its cost and the quantity available limit it as a substitute for zinc in galvanizing. Other metals, particularly aluminum, may be substituted for zinc coating on steel in some instances, but the cost to date has inhibited extensive use. Sheet aluminum is a strong competitor of galvanized steel, although it has poorer structural qualities and its cost in the same gage sheets is higher.

Aluminum alloys and stainless steel have replaced part of the brass formerly consumed by the building industry and thus have reduced the zinc market in the brass mills.

Aluminum competes with zinc in certain diecasting applications, the competition between the two metals being influenced in part by metal prices, but for the most part selection of an alloy depends upon the properties desired in the finished casting. In addition, where the use of electrodeposited coatings is desired, zinc has a great advantage because of the ease with which finishes can be applied over diecastings of zinc alloy. Acetate plastic moldings and steel stampings are strongly competitive with diecastings.

The competition of substitute materials is keenly felt in chemical and pigment uses. Aluminum and magnesium could replace zinc to some extent as reducing agents in chemical reactions. In the paint industry lead and titanium pigments are used instead of zinc pigments in many instances. Titanium pigments have almost wholly replaced lithopone, but supplement rather than compete with zinc oxide in most paint formulations. Titanium dioxide

has made inroads on the use of zinc oxide in porcelain enamels, and in opacifiers, zirconium compounds have partly replaced zinc oxide. Zinc oxide consumption per unit of rubber consumption has declined in recent years, not because of substitution of an alternate product but rather because the synthetic rubbers require little or no zinc oxide in the vulcanizing process.

Substitute materials exist for many zinc uses. Which material is used and in what amount depends upon cost factors, relative technologic advantage, and availability and stability of supply.

SECONDARY SOURCES AND RECOVERY

Secondary zinc is the total zinc in all forms recovered from old scrap and from such new scrap as enters trade for processing. Combined old and new scrap containing zinc, annually yields 250,000 to 300,000 tons of recoverable zinc as slab zinc, zinc dust, various alloys and pigments, and chemicals. Table 6 shows the kinds of scrap processed and the quantity of zinc recovered by product.

Zinc-base scrap is divided into new and old scrap. New scrap is defined as that generated in manufacturing processes and consumed at plants other than where generated. Old scrap consists of zinc, zinc products, or alloys which have been discarded because of wear, damage, or obsolescence.

Zinc dross, ashes, and skimmings produced in hot-dip galvanizing and continuous galvanizing lines account for about 50 percent of the zinc recovered from zinc-base scrap sources. Dross is a mixture of zinc-iron alloys which form in the galvanizing kettles through the interaction of hot zinc and steel or iron. The quantity of dross which settles out, differs with the type of work and the process. About 15 percent of total zinc consumed by job galvanizers is lost as dross, but individual plant losses range from 10 to 50 percent (*10*).

Zinc ashes, the zinc oxide which forms at the surface of the hot-dip galvanizing kettle accounts for losses ranging from about 3 to 20 percent depending on operating temperatures and percentage of standby time. Zinc losses in "sal" or flux skimmings range from about 2 to 5 percent of zinc put in the galvanizing kettle.

Sheet and strip continuous galvanizing lines introduced since World War II have eliminated a large part of the zinc losses in dross, ashes, and skimmings through the use of carefully controlled scale-free strip, use of aluminum in the galvanizing bath which minimizes formation of zinc-iron alloys, and by maintenance of nonoxidizing atmospheres which eliminates the necessity for flux and the formation of zinc oxide at the surface of the bath. Zinc losses as dross and skimmings in the continuous strip galvanizing mills are about 5 percent.

Other new zinc scrap includes die-cast skimmings, flue dust, and chemical residues. Chemical residues are generated as a byproduct

TABLE 6.—*Zinc recovered from scrap processed in the United States, by kind of scrap and form of recovery*

[Short tons]

Kind of scrap	1962	1963
New scrap:		
Zinc-base	109, 324	110, 886
Copper-base	87, 893	91, 592
Aluminum-base	2, 994	3, 144
Magnesium-base	53	69
Total	200, 264	205, 691
Old scrap:		
Zinc-base	33, 588	32, 572
Copper-base	25, 929	27, 634
Aluminum-base	2, 192	2, 302
Magnesium-base	44	56
Total	61, 753	62, 564
Grand total	262, 017	268, 255

Form of recovery	1962	1963
As metal:		
By distillation:		
Slab zinc [1]	58, 217	59, 540
Zinc dust	24, 497	23, 417
By remelting	3, 892	4, 317
Total	86, 606	87, 274
In zinc-base alloys	15, 183	14, 940
In brass and bronze	118, 487	125, 087
In aluminum-base alloys	5, 256	5, 543
In magnesium-base alloys	154	201
In chemical products:		
Zinc oxide (lead-free)	18, 985	18, 591
Zinc sulfate	(2)	(2)
Zinc chloride	11, 753	10, 768
Miscellaneous	5, 593	5, 851
Total	175, 411	180, 981
Grand total	262, 017	268, 255

[1] Includes zinc content of redistilled slab made from remelt die-cast slab.
[2] Included with "Miscellaneous."

in the manufacture of sodium dithionate (sodium hydrosulfite) used by the textile industry as a bleach and are high-grade scrap used in making high-quality zinc oxide. Sal skimmings, on the other hand, are frequently generated at a rate in excess of the market for the zinc chloride and zinc ammonium chloride made from the skimmings.

Zinc dust, redistilled zinc and to a lesser extent zinc oxide, are made from galvanizers' dross. Redistilled zinc, remelted die-cast slab, and zinc oxide are the principal products made from die-cast skimmings, die-cast scrap, and zinc flue dust. Distillations are usually made in clay or graphite vertical retorts.

The second and almost equally important source of secondary zinc is the copper-base alloys, brass and bronze. The contained zinc is almost wholly recovered in brass and bronze ingot and brass mill products, though a small part which accumulates as flue dusts may be recovered in other products.

Minor quantities of zinc are recovered in the utilization of scrap aluminum and magnesium-base alloys at light-metal foundries.

RESERVES

Zinc ore reserves are widely distributed throughout the world. Countries with important productive deposits include Algeria, Argentina, Australia, Bulgaria, Canada, the Congo (Leopoldville), Finland, West Germany, Italy, Japan, North Korea, Mexico, Morocco, Peru, Poland, Northern Rhodesia, Spain, Sweden, the United States, the U.S.S.R., and Yugoslavia.

Table 7 lists the measured and indicated reserves of zinc in ores inventoried or estimated, based on available data, existing prices and technologies as of January 1962. Reserves of inferred zinc are judged to be at least equal to the sum of measured and indicated reserves. Extraction of zinc using current mining, milling, and smelting practices would recover about 75 percent of the contained zinc.

TABLE 7.—*Estimate of world reserves of zinc in measured and indicated ore, January 1962* [1]

Country	Zinc content (thousand short tons)	Percent of total
North America:		
Canada [2]	19,000	22.3
Mexico	4,000	4.7
United States	12,200	14.4
South America: Argentina, Bolivia, Brazil, and Peru	6,000	7.1
Europe:		
Free world countries	13,000	15.3
Soviet-bloc countries	13,000	15.3
Africa: Algeria, Congo (Leopoldville), Egypt, Kenya, Morocco, Nigeria, Northern Rhodesia, South-West Africa, and Tunisia	4,500	5.3
Asia: Burma, China, India, Iran, Japan, North Korea, North Viet-Nam, Turkey	8,000	9.4
Australia [3]	5,300	6.2
Total	85,000	100.0

[1] U.S. Bureau of Mines 1957 survey with adjustments for later data.
[2] Canada Department of Mines and Technical Surveys, Mineral Information Bulletin, MR 53, 1961, p. 27.
[3] Australian Bureau of Mineral Resources (other reports quoting higher figures are believed to include inferred reserves).

CONSERVATION

Utilization of zinc resources in the production of zinc has been promoted by relevant research and application of the findings to the several phases of zinc production. Cutoff grades in mines are constantly adjusted to permit extraction of the lowest economic ore grade, and access to marginal grades of ore is maintained to the degree practical. Improved mining practice, particularly in ore bodies amenable to greater mechanization, has served to make large tonnages of lower grade ore profitable.

Continuing technologic advances in milling have had a tremendous impact in extending the world's economic resources in zinc. Chief among these was the development of selective flotation which made possible the production of high-grade concentrates with good recoveries. Another important development has been the introduction of heavy-medium concentration, which reduced overall treatment costs by rejection of a large part of the gangue fraction of the ore prior to grinding and beneficiation.

Conservation is also practiced in smelting. Sulfur dioxide gases from the roasting-sintering units are converted to sulfuric acid, and cadmium once marketed with slab zinc is recovered for its specialized uses. Residues containing zinc, lead, and other metal values are either treated for additional recoveries or are stocked for future processing. At present almost 10 percent of domestic slab zinc is produced from zinc-bearing slags at lead smelting plants.

Much of the zinc entering brass, bronze, and zinc- or light-metal casting alloys is ultimately recovered as secondary metal. That going into industry as galvanized steel or zinc oxide becomes so dispersed that no recovery is possible. The new scrap generated in the production of all zinc-bearing products is held at minimum levels by competition and is recycled to the secondary recovery plants for reclamation.

SOURCES OF STATISTICAL INFORMATION

The Bureau of Mines canvasses mine output of the principal mines, consumption of zinc-base scrap, and production of secondary zinc products, the output of zinc oxide, the consumption of slab zinc, and stocks of zinc held by consumers on a monthly basis. These data with smelter output and producers' stocks obtained

from the American Zinc Institute, import-export statistics from the Bureau of Census, and market information from the Engineering and Mining Journal Metal and Mineral Markets form the bases of comprehensive and adequate monthly statistics on the zinc industry.

Annual statistics are based on the same data, supplemented by annual reports covering mine, smelter, and rolling mill output, recovery of zinc from copper-, aluminum-, and magnesium-base scrap, and raw materials used and items produced by manufacturers of zinc pigments and salts. The annual statistics are further supplemented by world mine and smelter production by countries, the data being compiled by the Bureau of Mines from State Department dispatches, reports of foreign governments, and other sources.

The Mineral Census of the United States made in 1958 and 1962 provides valuable general information on productivity and costs. Special studies by the Tariff Commission in 1954, 1958, 1960, and 1962 have further added to available statistical information.

The Yearbook of the American Bureau of Metal Statistics contains tables of world zinc consumption by country and slab zinc capacity of individual smelters. The monthly bulletin of the International Lead and Zinc Study Group includes data on world metal stocks and trade movements of concentrates and metals. Publications such as the World Non Ferrous Metal Statistics (London), The Non Ferrous Metal Industry (Paris), and Metallgeselschaft (Frankfurt) gives the consumption of slab zinc by detailed use and other detailed data for a number of countries.

PRODUCTION, CONSUMPTION, AND TRADE

World mine and smelter production of zinc have increased almost without interruption since the end of World War II and in 1963 were 3.97 and 3.83 million short tons, respectively. These quantities are more than 50 percent above wartime outputs and more than double the production rates of 1945 and 1946.

Mine production of zinc in the United States reached 768,000 tons in 1942. After the war production ranged from 681,000 tons in 1951 to 412,000 tons in 1958, followed by a rising trend to 529,000 tons in 1963. Domestic smelters reached a record high of 991,000 tons in 1943 and 1,058,000 tons in 1957. After a slump to 828,000 tons the next year, a slow upward trend began with output reaching 953,000 tons in 1963.

In 1963 zinc mine production was recorded for 42 countries of which 26 had ouptut in excess of 10,000 tons of contained zinc. The four leading countries ranked in order were the United States, Canada, the U.S.S.R., and Australia; they had a combined output of 1,871,000 tons, 47 percent of the total. The United States exceeds all other countries in smelter output of zinc accounting for 23 percent in 1963. The U.S.S.R., Japan, Canada, and Belgium followed with 13, 8, 7, and 6 percent of the total, respectively. Twenty other countries supply the remaining 43 percent.

The United States in 1963 consumed 1.1 million tons of slab zinc, 29 percent of the world total. The U.S.S.R. consumed an estimated 410,000 tons. Other nations consuming in excess of 100,000 tons annually in order of demand are Japan, West Germany, United Kingdom, France, Belgium, Italy, and Australia.

In addition to consumption of slab zinc the United States annually consumes about 200,000 tons of recoverable zinc in scrap to produce zinc dust, pigments, chemicals, and alloys as shown in table 6. Yet another 100,000 to 110,000 tons of zinc in ore is used directly in making American process zinc oxide, lithopone, or chemicals. The sum of such consumption is the total consumption on figure 1, while consumption reported by industry products in table 10 is slab zinc only.

Domestic slab zinc consumption since World War II has fluctuated appreciably, but the trend shows an average annual increase of about 20,000 tons. Consumption was 801,000 tons in 1946, dropped to 712,000 tons by 1949, rose to a record 1,120,000 tons in 1955, slumped to 868,000 tons by 1958 and then rose to a new record of approximately 1,200,000 tons in 1964. Most of the growth is due to the increased consumption for zinc-base alloys from 212,000 tons in 1946 to 463,000 tons in 1963. Zinc consumed in galvanizing rose from 320,000 tons in 1946 to 451,000 tons in 1955, declined to 361,000 tons in 1954, and then increased to 420,000 tons by 1963. In brass products zinc consumption declined from 149,000 tons in 1946 to 130,000 tons in 1963 and in rolled zinc for the same period the decline was from 92,000 to 42,000 tons.

Before 1939, domestic mines provided most U.S. needs for zinc ore, and at times the United States exported substantial quantities of ore to other countries. After 1939, the United States became a large net importer of zinc ores and concentrates amounting to one-third of the ore supply between 1940 and 1949 and about one-half of the ore supply between 1954 and 1958. The trade in zinc metal followed a similar pattern except that a period of reversals between a net importing or exporting position occurred between 1938 and 1948 after which imports became increasingly important. By 1957 metal imports were equivalent to one-half of the quantity of zinc produced from domestic ore.

TABLE 8.—*Supply and distribution of slab zinc in the United States*

[Thousand short tons]

Year	Supply						Distribution		
	Primary production		Redistilled secondary	Total	General imports of slab zinc	Total	Consumption of slab zinc [1]	Exports of slab zinc	Total
	Domestic materials	Foreign materials							
1954–58 (average)	464	439	65	968	212	1,180	963	13	976
1959	348	450	58	856	157	1,013	956	12	968
1960	334	465	69	868	121	989	878	75	953
1961	413	434	55	902	128	1,030	931	50	981
1962	448	431	59	938	142	1,080	1,032	36	1,068
1963	474	419	60	953	145	1,098	1,105	34	1,139

[1] Includes small quantity of remelt zinc.

TABLE 9.—*Mine production of recoverable zinc in the United States, by States*

[Short tons]

State	1954–58 (average)	1959	1960	1961	1962	1963
Arizona	26,432	37,325	35,811	29,585	32,888	25,419
Arkansas		49	50	37	211	
California	3,864	78	465	304	322	101
Colorado	38,976	35,388	31,278	42,647	43,351	48,109
Idaho	54,392	55,699	36,801	58,295	62,865	63,267
Illinois	21,458	26,815	29,550	26,795	27,413	20,337
Kansas	19,133	1,017	2,117	2,446	3,943	3,508
Kentucky	594	673	869	1,147	1,172	1,461
Missouri	3,476	92	2,821	5,847	2,792	321
Montana	56,764	27,848	12,551	10,262	37,678	32,941
Nevada	3,315	217	420	453	281	571
New Jersey	13,373			112	15,309	32,738
New Mexico	18,401	4,636	13,770	22,900	22,015	12,938
New York	56,600	43,464	66,364	54,763	53,654	53,495
North Carolina						13
Oklahoma	26,489	1,049	2,332	3,148	10,013	13,245
Oregon				3		3
Pennsylvania	2,162	16,718	13,746	23,428	24,308	27,389
Tennessee	46,752	89,932	91,394	81,734	71,548	95,847
Texas						
Utah	41,158	35,223	35,476	37,239	34,313	36,179
Virginia	19,163	20,334	19,885	29,163	26,479	23,988
Washington	24,049	17,111	21,317	20,217	21,644	22,270
Wisconsin	18,293	11,635	18,410	13,865	13,292	15,114
Total	494,844	425,303	435,427	464,390	505,491	529,254

TABLE 10.—*Consumption of slab zinc in the United States, by industries*

[Short tons]

	1954–58 (average)	1959	1960	1961	1962	1963
Galvanizing	408,547	361,027	371,589	382,077	388,570	420,287
Brass products	118,456	129,278	99,023	128,523	129,805	128,237
Zinc-base alloys	355,006	389,331	338,373	341,766	423,608	468,619
Rolled zinc	45,664	42,949	38,696	41,204	42,233	42,166
Zinc oxide	18,811	18,248	15,593	18,137	18,517	16,037
Other products	16,886	15,364	14,610	19,506	29,088	29,767
Total	963,370	956,197	877,884	931,213	1,031,821	1,105,113

TABLE 11.—*General imports of zinc in ores, blocks, pigs, or slab zinc into the United States, by country*

[Short tons]

	1954–58 (average)	1959	1960	1961	1962	1963
Ores (zinc content):						
Australia	7, 849	24, 693	17, 789	3, 822	10, 956	3, 724
Canada	164, 160	152, 134	120, 336	119, 113	192, 423	134, 303
Bolivia	7, 106	2, 530	1, 214	572	1, 791	4, 395
Guatemala	7, 867	8	6, 063	13, 870	2, 511	1, 430
Mexico	181, 258	182, 409	190, 621	186, 174	165, 005	138, 185
Peru	99 533	86, 672	80, 100	74, 369	77, 501	73, 788
South Africa, Republic of	13, 076	7, 957	12, 300	7, 551	9, 589	8, 614
Other	8, 430	43, 712	28, 732	10, 229	7, 622	8, 330
Total	489, 279	500, 115	457, 155	415, 700	467, 398	372, 769
Blocks, pigs, or slabs:						
Belgium-Luxembourg	22, 702	7, 666	5, 724	12, 854	23, 232	21, 904
Canada	106, 574	88, 414	74, 168	71, 628	72, 825	73, 817
Congo (Léopoldville)	20, 181	12, 790	9, 307	11, 420	10, 882	9, 590
Germany, West	7, 296	55	2, 680	779	1, 162	6, 103
Italy	8, 228	7, 459	3, 517	1, 820	992	907
Mexico	18, 630	9, 338	8, 950	8, 598	12, 334	13, 219
Peru	11, 159	12, 337	7, 517	7, 519	7, 615	7, 574
Northern Rhodesia	1, 825	4, 667	615	1, 400	4, 643	1, 982
Spain			2, 986	6, 756	2, 572	6, 270
Yugoslavia	3, 438	3, 643	4, 520	3, 198	3, 310	1, 185
Other	12, 315	10, 594	783	1, 590	2, 390	2, 206
Total	212, 348	156, 963	120, 767	127, 562	141, 957	144, 757

Source: Bureau of the Census.

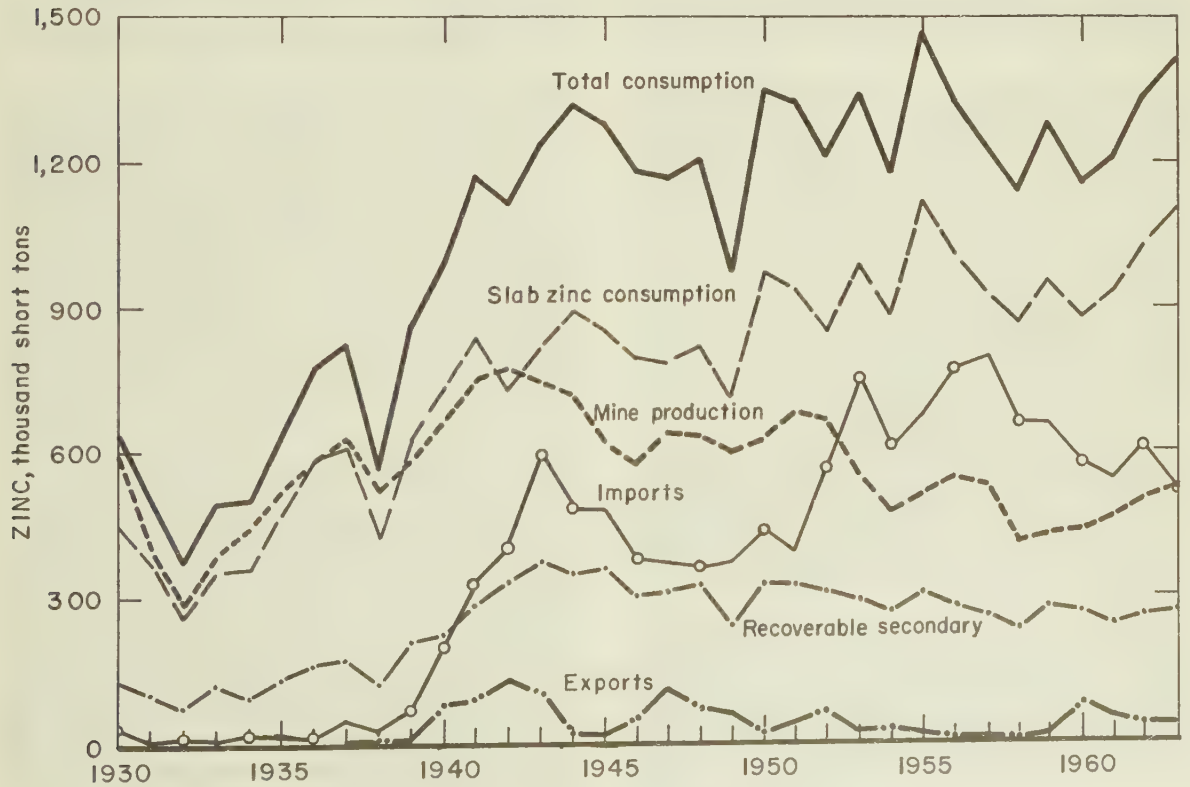

FIGURE 1.—Sources of Zinc Supply and Consumption in the United States.

TABLE 12.—*World mine production of zinc (content of ore)*[1] *by countries*

[Short tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963
Algeria	34, 538	42, 774	44, 240	46, 448	46, 215	40, 000
Argentina	28, 594	44, 974	39, 022	35, 502	34, 686	31, 600
Australia	307, 470	308, 373	355, 497	348, 496	378, 042	394, 326
Bulgaria	44, 974	75, 508	84, 878	81, 461	69, 125	63, 831
Canada	414, 264	[2] 396, 008	[2] 406, 873	443, 099	501, 937	497, 180
China (estimate)	37, 000	70, 000	90, 000	110, 000	110, 000	110, 000
Congo (Leopoldville)	108, 137	78, 313	120, 352	109, 828	105, 530	114, 139
Finland	34, 050	59, 588	46, 328	51, 363	57, 509	73, 142
France	13, 711	17, 616	18, 933	17, 284	15, 735	17, 734
Germany, West	101, 114	90, 566	95, 159	96, 189	95, 991	102, 722
Greece	10, 400	13, 200	16, 200	19, 342	18, 939	20, 100
Italy	138, 750	146, 089	143, 985	147, 954	145, 596	117, 900
Japan	136, 695	156, 899	172, 769	185, 474	212, 174	218, 195
Korea, North (estimate)	70, 000	95, 000	95, 000	100, 000	100, 000	120, 000
Mexico	266, 535	290, 938	289, 274	296, 492	276, 330	265, 763
Morocco	48, 053	61, 301	54, 199	44, 951	37, 942	36, 420
Norway	7, 617	10, 907	11, 395	10, 285	12, 566	13, 700
Peru	174, 049	[2] 157, 739	[2] 196, 346	[2] 191, 658	[2] 178, 839	[2] 200, 030
Poland	166, 184	142, 529	158, 843	153, 857	159, 961	162, 150
Northern Rhodesia	36, 866	46, 497	49, 242	45, 100	45, 100	42, 100
Spain	95, 011	94, 645	94, 920	96, 983	86, 554	98, 786
South-West Africa [2]	21, 124	12, 394	13, 119	14, 905	25, 201	36, 871
Sweden	70, 870	86, 549	81, 824	87, 558	69, 856	73, 700
U.S.S.R. (estimate)	[3] 300, 000	[2] 370, 000	[2] 380, 000	[2] 440, 000	[2] 450, 000	[2] 450, 000
United States [2]	494, 844	425, 303	435, 427	464, 390	505, 491	529, 254
Yugoslavia	64, 501	66, 882	62, 150	66, 009	67, 367	56, 511
Other countries	90, 737	65, 312	91, 255	95, 263	74, 271	72, 031
Total [4]	3, 330, 000	3, 440, 000	3, 660, 000	3, 810, 000	3, 890, 000	3, 970, 000

[1] Data derived in part from the Yearbook of the American Bureau of Metal Statistics, the United Nations Statistical Yearbook, and the Statistical Summary of the Mineral Industry (Overseas Geological Surveys, London).

[2] Recoverable.

[3] Smelter production.

[4] Czechoslovakia and Rumania also produce zinc, but production data are not available; estimates are included in totals.

Depressed conditions in the domestic zinc industry led to imposition of import quotas, effective October 1958, on zinc metal and ore. The annual quotas were set at 80 percent of the U.S. average annual commercial import rate from 1953 through 1957—379,840 tons of zinc in ore (concentrates) and 141,120 tons of zinc in metal. At the start of 1965 the quotas remained in effect and the Tariff Commission was preparing a report following an investigation on the condition of the zinc industry with particular reference to the quota system.

Of the 2,248,000 tons of zinc imported from 1960 through 1963, 76 percent has been as concentrates and 24 percent as metal. Mexico, Canada, and Peru supplied 40, 33, and 18 percent, respectively, of the zinc as concentrates. Canada, Belgium-Luxembourg, and Mexico supplied 55, 12, and 8 percent, respectively, of the zinc as metal.

Exports of zinc metal were 107,000 tons in 1947, but declined thereafter to 2,000 tons in 1958. After imposition of quotas a practice of smelting ex-quota ore in bond for export developed, and in 1960 exports were 75,000 tons followed by a decline to 34,000 tons in 1963. Much of the exports have been to Latin American countries, India, and the Republic of Korea.

Zinc is also exported as scrap, as sheets, plates, and strips, as zinc dust, and in pigments and salts as well as in fabricated metal products.

Imported zinc has been subject to tariff regulation since 1846 (*14*). The highest rates were in effect from 1930 to 1939 when the duties on slab zinc and ores and concentrates (zinc content) were 1.75 and 1.50 cents per pound, respectively. Since that time the duties on slab and zinc in ore have been progressively reduced so that by June 6, 1951, import duties on slab and ore were 0.7 and 0.6 cent per pound, respectively. These rates were suspended during the period of February 12 through July 23, 1952.

New tariff schedules which went into effect August 31, 1963, revised the method of computing duties on zinc ores and concentrates. Under the new schedules the rate of duty became 0.67 cents per pound imposed on the zinc content after certain allowable deductions for processing losses. For a given importation the net result was a total duty approximately the same as under the previous method.

TABLE 13.—*World smelter production of zinc, by countries* [1]

[Short tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963
Argentina	15,355	14,440	17,637	15,873	18,487	21,716
Australia	142,270	130,436	134,658	155,270	188,079	201,349
Austria	[2] 6,283	12,608	12,700	13,302	13,325	13,074
Belgium [3]	243,859	247,250	272,891	270,670	227,248	227,437
Bulgaria	[2] 6,323	10,024	18,639	24,385	57,017	61,800
Canada	252,976	255,306	260,968	268,007	280,158	283,380
China (refined) (estimate)	35,000	65,000	75,000	100,000	100,000	100,000
Congo (Leopoldville)	46,448	60,418	58,817	62,788	61,759	58,118
France	135,446	164,817	168,709	183,615	185,388	186,392
Germany:						
East				1,102	5,512	11,000
West	187,232	152,046	156,299	155,373	143,127	115,969
Italy	77,856	81,517	88,040	86,424	85,618	81,093
Japan	138,818	175,642	198,920	234,163	270,402	291,381
Korea, North (estimate)	[4] 13,000	27,000	55,000	65,000	65,000	70,000
Mexico	62,035	61,362	58,318	57,119	62,730	62,557
Netherlands	30,880	35,445	39,771	43,643	40,839	39,421
Norway	51,285	53,767	48,460	51,287	49,576	49,214
Peru	22,134	29,595	35,712	35,006	35,566	60,312
Poland	170,414	185,263	193,501	200,633	199,935	199,739
Northern Rhodesia	32,159	33,483	33,369	33,444	44,576	54,509
Spain	25,741	27,039	49,565	57,865	68,981	70,778
U.S.S.R. (estimate)	300,000	400,000	435,000	470,000	510,000	510,000
United Kingdom	88,598	81,722	83,220	104,031	108,949	110,911
United States	903,316	798,666	799,516	846,795	879,395	892,584
Yugoslavia	23,804	35,220	39,612	40,640	43,325	46,566
Total [5]	3,020,000	3,150,000	3,350,000	3,590,000	3,750,000	3,830,000

[1] Data derived in part from the Yearbook of the American Bureau of Metal Statistics, the United Nations Statistical Yearbook, and the Statistical Summary of the Mineral Industry (Overseas Geological Surveys, London).

[2] Average annual production 1955–58.

[3] Includes production from reclaimed scrap.

[4] Average annual production 1957–58.

[5] Czechoslovakia and Rumania also produce, but production data not available; estimates in total.

In terms of an equivalent ad valorem base the duty on zinc in concentrate has been reduced from approximately 56 percent in 1930 to 10 percent in 1963; that on slab zinc in the same period declined from 38 to 6 percent.

On September 22, 1958, the President acting on recommendations of the Tariff Commission proclaimed imposition of import quotas on zinc (and lead) effective October 1. The quotas established were 80 percent of the average dutiable imports into the United States during the base period, 1953–57, and duty rates remained at then existing levels (*15*).

STRATEGIC CONSIDERATIONS

The United States was fully self-sufficient in zinc supplies until about 1940. Since then increased consumption, decreased mine production, and diversion of substantial quantities to build a national stockpile in the period 1949–59 brought about partial dependence on imports. Between 1942 and 1958, 35 percent of all supply was from imports. In the period 1954–58 about 45 percent of the U.S. supply was imported. These quantities exceeded requirements by a large margin which was added to industry and government stocks. Imports needed to balance consumer requirements in the 5 years, 1954–58, averaged 500,000 short tons. Average annual imports for the period were 702,000 tons of which 653,000 tons was slab zinc, or recoverable as such, or an annual excess of 153,000 tons. Imports needed to balance consumer requirements in the 5 years 1959–63, averaged 544,000 tons. Average annual imports were 581,000 tons of which 541,000 tons was slab zinc, or recoverable as such, a quantity approximately equal to reported requirements.

Mining and smelting capacities to produce zinc, imports expected from strategically accessible foreign sources, and the zinc in the Nation's stockpile are calculated to be adequate to meet any anticipated wartime requirements. Primary and secondary zinc producing plants and stockpiled zinc are well dispersed. Furthermore, the chief source of imports, neighboring Canada and Mexico, produce large quantities of zinc in excess of their requirement and both are accessible by rail, as well as ocean freight. Imports from Western Hemisphere countries in 1959 through 1963 amounted to about 85 percent of the import requirements for consumption.

GOVERNMENT PROGRAMS

The defense program of the United States relating to zinc was authorized by the Strategic and Critical Materials Stockpiling Act of 1946 (Public Law 520, 79th Cong.) and the Defense Production Act (DPA) of 1950, as amended.

TABLE 14.—*Zinc tariffs under the Tariff Act of 1930 and the Reciprocal Trade Agreements Act*

[Cents per pound]

	Tariff Act of 1930	Canadian Agreement, Jan. 1, 1939	Geneva Agreement, Jan. 1, 1948	Torquay Agreement, June 6, 1951
Zinc-bearing ores, except pyrites containing not more than 3 percent zinc (rates apply on zinc content)	$1.50	$1.20	$0.75	[1] $0.60
Zinc in blocks or slabs	1.75	1.40	.87½	.70
Zinc sheets	2.00	2.00	1.00	1.00
Zinc oxide and leaded zinc oxides containing not more than 25 percent lead	1.75	1.75	.60	.60
Lithopone containing less than 30 percent of zinc sulfide	1.75	[2] 1.50	.87½	.87½

[1] New tariff schedules, effective Aug. 31, 1963, changed rate to .67 cents on assay zinc content less certain allowable deductions to remain approximately equivalent to the previous rate.
[2] Netherlands Agreement, Feb. 1, 1936.

The stockpiling act authorized and directed the determination of an acquisition of quantities of metals deemed necessary to the public defense, and under its provisions stocks held by the Metals Reserve Co. were transferred to the national stockpile in 1948. DPA purchases in substantial quantities began in 1949. The 1.5 million tons of zinc initially established as an objective was revised downward to 700,000 tons in 1951. Upward revisions in 1954 and 1956 brought the objective to 1.2 million tons, but objectives were reduced to 178,000 tons in 1958 and eliminated in 1963. On June 30, 1964, government inventories totaled 1.6 million tons, of which 1.3 million was in the national (strategic) stockpile and 0.3 million in the supplemental stockpile.

Under authority of Public Law 480 (1954) and Office of Defense Mobilization (ODM) authorization of May 1956, The Department of Agriculture, through its agent, the Commodity Credit Corporation, traded perishable surplus agricultural products for zinc of foreign origin. The 327,000 tons of zinc acquired from 1956 through 1960 under this program was placed in the supplementary stockpile.

Under the Defense Production Act of 1950, as amended, the Defense Minerals Exploration Administration (DMEA) was authorized to grant loans up to 50 percent of approved costs on exploration of zinc. Public Law 85–701 (1958) established the Office of Minerals Exploration (OME) in the Department of the Interior as the successor to the DMEA. Zinc was removed effective July 1, 1962, from the list of metals eligible for exploration assistance under the program. Through 1963, DMEA and OME had entered into 290 contracts for exploration of zinc and/or lead. The total estimated cost was $27.4 million of which the Government's share was $13.7 million. Exploration was judged to be successful on 86 properties. ore discoveries ranging from several hundred tons of ore to one of 35 million tons in eastern Tennessee.

PRICES AND COSTS

Market prices of zinc are established by the producer and most commonly quoted in cents per pound for Prime Western Grade, f.o.b., East St. Louis, although relatively little zinc is delivered there; Brass Special and Intermediate grades are normally quoted ¼ and ½ cents, respectively, above the Prime Western Grade. These grades of zinc are also quoted on a delivered basis that is ½ cent above the East St. Louis price. High Grade and Special High Grade are quoted on a delivered basis at approximately 1¼ and 1½ cents per pound above the East St. Louis price of Prime Western.

The London Metal Exchange (LME), founded in 1881, is another important market pricing center. Although relatively small quantities of zinc are sold on the exchange, the quotations are widely used as a basis for pricing large quantities of zinc and zinc ores sold outside the exchange. In 1964 many producers outside the United States have also established a producer price.

Since 1951 various supply and demand factors have caused the price to decline from a high of 19.5 cents in May 1952 to 9.25 cents a pound in 1954. Following the 1954 low, prices advanced to 13.5 cents in 1955, declined to 10.0 cents in 1957, and then upward to 14.5 cents in October 1964.

The price data given in table 15 permit comparison of the price of Joplin concentrate with refined common zinc in St. Louis, New York,

TABLE 15.—*Prices of zinc*

	1959	1960	1961	1962	1963
Joplin 60-percent zinc concentrate: [1] Price per short ton, dollars	67.53	79.67	68.42	69.00	72.01
Average price common zinc at:					
St. Louis (spot) [1] cents per pound	11.46	12.95	11.55	11.63	12.01
New York [1] do	11.96	13.45	12.05	12.13	12.51
London [2] do	10.27	11.05	9.78	8.43	9.60

[1] Metal Statistics, 1964.
[2] E&MJ Metal and Mineral Markets English quotations converted into American money on basis of average rates of exchange recorded by Federal Reserve Board.

and London. Evaluation of the tabulation reveals the substantial increase in the percent of metal price paid for the zinc contained in concentrate as the metal price increases. The table also shows that the LME price has generally been about 2 to 3 cents below the New York price, the difference largely representing the added costs of duty, ocean freight, and insurance for delivery to the United States.

TAXES

The zinc mining industry receives the maximum depletion allowance for metallic minerals of 23 percent on domestic production and 15 percent on foreign production.

TRANSPORTATION

Zinc ore is usually concentrated at mills situated in close proximity to the mines. Exceptions are or have been the Butte-Anaconda, Montana operation where ore is hauled by rail about 26 miles to the concentration plant at Anaconda; the Midvale mill at Midvale, Utah; the Eagle-Picher Central mill at Cardin, Okla.; and the Eagle-Picher mill north of Galena, Ill. Concentrate of domestic and foreign origin is transported by rail, truck, or boat to smelters. In 1961, examples of the freight rate per ton of concentrate shipped by rail to the smelter were $0.50 from the Summit Valley district to Anaconda, Mont.; $1.08 from Coeur d'Alene, Idaho to Kellogg, Idaho; $6.61 from Lawrence County, N.Y. to Josephtown, Pa.; $8.42 from eastern Tennessee to East St. Louis, Ill.; and $20.74 from Central, N. Mex. to Palmerton, Pa.

RESEARCH

Research plays a vital role in maintaining zinc in a competitive position with alternate materials. These research efforts by individual companies, trade associations, and government agencies are directed towards all phases of the zinc industry—ore discovery, production, and product utilization.

Exploration efficiency has been advanced by studies of the geological controls involved in the process of ore deposition and by developing improved methods such as the use of photogeology, geochemistry, and various geophysical techniques. These methods have been successful in discovering new mineral districts as well as extending old districts.

Research in mining has emphasized development of equipment to mechanize operations or otherwise increase labor productivity to offset rising prices of wages and supplies. Bureau of Mines mining research includes studies of hydraulic stope filling, roof-control, rock mechanics, rock drilling, and statistical analysis for operational control.

In minerals beneficiation much of the research has been directed towards improvement of equipment and operating practices. Notable advances are in progress to monitor or control milling processes by automatic systems such as sound measuring instruments for grinding mill loads, gamma-ray density meters for pulp density, torque measurements for classifier sand return, and fluorescent X-ray spectrometry for reagent control in flotation. The Bureau of Mines ore beneficiation studies include the use of radioactive tracers in mill processes and recovery of zinc concentrates from complex ores, slimes, and mill tailings by flotation.

In zinc production research, the Imperial Smelting Corp., Ltd. achieved reduction of zinc in 1950 by use of a blast furnace with a number of attendant efficiencies. This type of furnace has since been built or scheduled for construction in eight countries. Other improvements have been made in roasting, sintering, and furnace design. The Bureau of Mines extractive studies include leaching with chemical solutions and microorganisms; reduction of sulfide minerals with atomic hydrogen; and use of vacuum and carrier gas distillation to improve separation and purification of metals.

Research on utilization of zinc has been carried on by many producers and some of the larger consumers of zinc. Development of diecasting alloys by The New Jersey Zinc Co. was a notable example. Beginning in 1958 many major zinc producers in the world working through the American Zinc Institute began a unified research program on zinc utilization. This research group changed its name July 1, 1963 from the Expanded Research Program of the American Zinc Institute and the Lead Industries Association to the International Lead-Zinc Research Organization (ILZRO). Included in the many research projects sponsored by ILZRO are new diecasting alloys, use of powder metal materials, welding of galvanized sheets, effect of temperature on properties of galvanized steel, cathodic protection of installations with zinc anodes, improved zinc-rich paints, and anodized finishes on zinc products.

Both zinc and zinc oxide readily form crystals that exhibit a wide spectrum of solid-state properties and have therefore received much attention by investigators of the fundamental properties of all substances.

An extensive library and information service is maintained by the American Zinc Institute. This association and the Zinc Development Association (London) jointly publishes Zinc Abstracts monthly giving a comprehensive coverage of zinc technology reported in the scientific and technical press.

OUTLOOK

The long-term upward trend of domestic slab zinc consumption should continue with an increase from the 1.1 million tons recorded in 1963 to 1.3 million tons by 1970 and 1.6 million tons by 1980. The forecast growth rate is somewhat more optimistic than a straight projection of zinc consumption data but is below a projection of the gross national product index.

Free world slab zinc consumption should increase approximately parallel to the United States, advancing from 3 million tons in 1963 to about 4 million tons by 1970. The Asian countries of India and Japan and a number of African countries are expected to experience significantly higher than average percentage increases, but their combined total consumption will still represent only about 15 percent of the free world total by 1970.

The use pattern of zinc in the United States should remain unchanged, except that the consumption of slab zinc for galvanizing and for diecasting will likely increase at a somewhat faster rate than for the other remaining use categories. An important factor in the long-term demand for zinc is the growing recognition of the value of protecting iron and steel products from corrosion by using a zinc coating. In the rapidly expanding die-cast and molded products field, zinc-base alloys can be expected to participate in the increase despite strong competition from other materials. The new alloy developments for rolled zinc may promote an upward trend of zinc consumption for this category. Increased use of zinc oxide for photocopying and other electronic applications utilizing the property of electro-luminescence also could add to the relatively stable older applications. The other numerous products consuming zinc do not have developments indicating any substantial future changes to their consumption pattern.

The increasing supply requirements will be met in part by an increase in domestic mine output from 530,000 tons of recoverable zinc in 1963 to a forecasted 620,000 to 650,000 tons by 1970 and probably somewhat in excess of this level thereafter. Relaxation of the import quota restrictions would undoubtedly result in larger imports of both concentrates and metal, particularly from Canada. There are substantial quantities of zinc in the national stockpile declared surplus to defense needs that must be taken into account as a significant factor in potential sources of supply for future years.

States east of the Mississippi River are expected to expand their zinc mine output from 51 percent of the total in 1963 to around 55 percent by 1970. The remaining production will be derived largely from the Western States with only a minor quantity from the West Central States. Replacement ore bodies, like those of east Tennessee and the Metaline area in Washington which are amendable to mechanized mining methods, and ore bodies with significant quantities of gold, silver, and copper will continue to compete successfully with foreign deposits. The trend toward vertical integration of domestic mining, smelting, and manufacturing companies will continue.

Domestic smelters will modestly increase slab zinc output to the extent practicable by available concentrates. Larger quantities of die-cast scrap should become available and be a larger factor in the production of slab zinc, zinc oxide, and other zinc products. There is a decided trend toward the higher grades of zinc making up a larger proportion of total output.

PROBLEMS

Producers, and indirectly the consumers, of zinc are confronted with technical and economic problems related to the discovery of new deposits, mining, milling, and smelting operations, and the marketing of zinc. Problems also occur because changes in policy by governments of major zinc producing countries require adjustments by the zinc industries in all affected countries.

The trend towards establishment of zinc reduction plants in countries previously only mining zinc causes disruption in trade patterns, especially in the supply of concentrates to the United States and Europe. New import sources of concentrate must then be found or greater effort directed toward replenishment of depleted domestic reserves, to supply the domestic smelters.

Better knowledge of geological ore depositional controls is required to aid in selecting areas for conducting exploration. Techniques are not adequate to utilize fully the exploration data and determine characteristics of the deposit important to future mining activity such as ease of drilling and breaking the rock, water flow expected, and stability of the mine structure.

Output at current and projected rates requires operation of some mines at increasing depths resulting in conditions of high rock pressures and temperatures, and the removal of water under a large pumping head. The lack of

knowledge of earth physics impedes solution of the problems of rock bursts, ground control, and water control. The shallow replacement-type deposits have similar, albeit not as dramatic problems. Additionally, breaking, loading, and hauling costs per ton of ore must be kept down since the average metal content of these latter deposits is usually low.

Loss of zinc through the combined steps of mining, milling, and processing is too high from the standpoint of both operating efficiency and conservation of resources. More knowledge of the physicochemical nature of complex mineral assemblages and of the ore beneficiating processes used would make possible an improved separation. In reduction of zinc concentrate to metal both basic and applied research is needed to reduce the processing cost.

The character of zinc scrap being generated is changing, requiring new types of treatment. The zinc dross from the continuous galvanizing lines has a higher aluminum content and possibly different physical properties than dross from previous processes, causing problems for secondary metal producers. Scrap zinc die-castings will be available in increasing quantities with attendant technologic and marketing problems.

As a counterpart to the supply side of the equation, there is an equal need to investigate the properties of zinc to assure full and wise utilization of the material. Although zinc has been in use for many centuries, voids remain in the knowledge regarding its physical and chemical properties. For example, zinc exhibits low creep resistance and also a low ductility at or below room temperature, both poor qualities for wrought-metal use. Little is known about the basic mechanism or the means of changing these properties by alloying.

Increased understanding of zinc for corrosion protection is needed. In the hot-dip galvanizing process, the effect on corrosion or weldability characteristics of the iron-zinc intermetallic substrate underlying the zinc coating is not clearly understood. On the atmosphere side of the coating, there is a need to minimize corrosion of the zinc.

Threshold knowledge indicates zinc oxide and other zinc compounds may be extremely useful in applications involving electroluminescence, photoconductivity, semiconductivity, or other electronic uses. However, much additional knowledge is needed on the thermodynamic, physical, and electronic properties of the compounds.

Other areas in which information is incomplete include the corrosion properties of zinc in various media; the energy requirements for rolling, extruding, joining, or other fabricating techniques; the function of zinc oxide in ceramics and glasses; and the utilization of zinc compounds in preventing mildew and in agricultural soil additives.

Continuing efforts are required to achieve orderly zinc marketing and price stability so that both producers and consumers can make plans with a reasonable assurance of future conditions. A major problem exists in determination of the zinc price at which substitution of alternate competitive materials is not a serious threat to zinc consumption and yet is sufficient to provide incentive for sustained output to meet the demand. Evaluation of the many world supply and demand factors is required for determination of the best commercial and government policies to attain this marketing goal.

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ZIRCONIUM

By Donald E. Eilertsen [1]

DUCTILE ZIRCONIUM, developed only about 10 years ago, is used in nuclear reactors and to resist attack by acid and alkaline solutions in industry.

Zirconium was discovered in 1789, and approximately 150 years later the zirconium industry emerged as a commercial enterprise in the United States. Zirconium was wanted for testing in nuclear reactors. The Bureau of Mines in cooperation with the Atomic Energy Commission (AEC) developed a large-scale production procedure for zirconium and shortly thereafter industry adopted the method. Zirconium sponge output reached a record 1,700 tons in 1961.

Zircon, dredged from sand deposits, is used commercially to produce zirconium metal, alloys, and compounds, but the largest use of zircon is in refractories, particularly foundry sand, and in abrasives and ceramics.

In the United States, three firms produce zircon, four firms process zircon to zirconium, and several firms produce zirconium alloys. Zircon and zirconia refractories are produced by approximately 12 firms. Numerous foundries use zircon as foundry sand.

Large quantities of zircon are consumed in the United States; much of this is imported, particularly from Australia. U.S. zircon resources are large but most would be expensive to recover.

The principal problem of the zirconium industry is: How can larger markets be developed for the metal?

BACKGROUND

Zirconium was prepared in elemental form in 1824, produced in relatively pure form in 1914, and made into high-purity grade in 1925 by the deBoer-van Arkel procedure. This procedure later was used for the first commercial zirconium production in the United States.

The Bureau of Mines began research on producing high-purity zirconium on a commercial scale in 1944 under the direction of W. J. Kroll. A method was developed and tested commercially to produce high-purity zirconium by the magnesium reduction of zirconium tetrachloride in an inert atmosphere. Private industry adopted this process in 1953, and soon afterwards the zirconium industry expanded and was able to produce large quantities of high-purity and commercial-grade zirconium. The AEC contracted for most of this zirconium for nuclear reactor testing and application. These contracts terminated in 1963, leaving the industry with idle capacity since zirconium's largest use is in nuclear reactors.

[1] Commodity specialist.

SIZE, ORGANIZATION, AND GEOGRAPHIC DISTRIBUTION OF THE INDUSTRY

Three firms in the United States produce zircon as a coproduct in mining heavy mineral sands for ilmenite and rutile. These companies are E. I. du Pont de Nemours & Co., Inc., at its Trail Ridge and Highland mines near Starke, Fla.; Titanium Alloy Manufacturing Division of National Lead Co. at the Skinner mine near Jacksonville, Fla.; and Florida Mineral Co. at its Vero mine at Vero Beach, Fla. Figures on zircon output are withheld because they are company confidential data.

Four firms produce zirconium sponge: U.S. Industrial Chemicals Co., Division of National Distillers & Chemical Corp., Ashtabula, Ohio; The Wah Chang Corp., Albany Division, Albany, Oreg.; The Carborundum Metals Co. Division, The Carborundum Co., Parkersburg, W. Va., and Akron, N.Y.; and Columbia-National Division, Pittsburgh Plate Glass Co.,

Pace, Fla. The latter firm placed its zirconium production facilities in a standby condition in mid-1963 for an indefinite period. Annual output of zirconium sponge in recent years has been in excess of 1,000 tons.

Zirconium sponge is converted to ingot by The Carborundum Metals Co. Division, The Carborundum Metals Co., Parkersburg, W. Va., and Akron, N.Y.; The Wah Chang Corp., Albany, Oreg.; Bridgeport Brass Co., Niles, Ohio, and U.S. Industrial Chemicals Co., Ashtabula, Ohio (divisions of National Distillers and Chemical Corp.); Harvey Aluminum, Inc., Torrance, Calif.; and Oregon Metallurgical Corp., Albany, Oreg. Annual production of zirconium ingot has been about 1,000 tons.

The principal producers of zirconium alloys are Union Carbide Corp., Metals Division, Alloy, W. Va., and Niagara Falls, N.Y.; Titanium Alloy Manufacturing Division of National Lead Co., Niagara Falls, N.Y.; and Vanadium Corporation of America, Cambridge, Ohio.

Titanium Alloy Manufacturing Division of National Lead Co., Niagara Falls, N.Y.; the Norton Co., Huntsville, Ala.; Harbison-Carborundum Co., Falconer, N.Y.; Zirconium Corporation of America, Solon, Ohio; and Tizon Chemical Corp., Flemington, N.J., process zircon to zirconium chemicals, principally zirconia. Annual zirconium oxide output, excluding that produced for zirconium metal production, has averaged about 5,000 tons in recent years.

Twelve firms processed zircon to refractories in 1963. The largest producers of refractories were Corhart Refractories Co. at Louisville, Ky., and Buckhannon, W. Va.; Harbison-Carborundum Corp., Falconer, N.Y.; The Charles Taylor Sons Co., Cincinnati, Ohio, and South Shore, Ky.; Walsh Refractories, St. Louis, Mo.; and Remmey Division of A. P. Green Fire Brick Co., Philadelphia, Pa. Annual zircon and zirconia refractory production has been between 21,000 and 37,000 tons in recent years.

Approximately 20 dealers in the United States sell domestic and imported zircon to consumers, the largest quantity going to the foundries.

DEFINITION OF TERMS, GRADES, AND SPECIFICATIONS

Domestic zircon ($ZrSiO_4$) is quoted on a minimum basis of 66 percent ZrO_2 content (98.2 percent pure zircon), while imported zircon is quoted on a minimum basis of 65 percent ZrO_2 (96.7 percent pure zircon).

Zirkite is a trade name for a mixture of zircon and baddeleyite.

Typical spectrographic analyses of the maximum impurities in nuclear-reactor-grade and commercial-grade zirconium sponge and zirconium oxide produced by The Wah Chang Corp. follow:

Impurities	Maximum impurities, parts per million		
	Nuclear-grade zirconium sponge	Commercial-grade zirconium sponge	Zirconium oxide
Aluminum	50	300	100
Boron	<.2	<.2	2
Cadmium	<.2	<.2	----
Calcium	<50	<50	----
Carbon	100	100	----
Chlorine	500	500	----
Chromium	70	70	30
Cobalt	<5	<5	<5
Copper	<20	<20	<20
Hafnium	7	25,000	80
Iron	800	800	1,000
Lead	10	10	<5
Magnesium	400	400	<20
Manganese	25	25	<10
Molybdenum	<10	<10	<10
Nickel	<10	<10	----
Nitrogen	25	50	<10
Oxygen	900	900	----
Silicon	70	70	300
Tin	----	----	<5
Titanium	<20	50	30
Tungsten	<50	<50	----
Vanadium	<20	<20	<20

Zircaloy-1 is an alloy of sponge zirconium containing, by weight, 2.5 percent tin.

Zircaloy-2 is an alloy of sponge zirconium containing, by weight, 1.2 to 1.7 percent tin, 0.7 to 0.20 percent iron, 0.05 to 0.15 percent chromium, and 0.03 to 0.08 percent nickel (*5*).[2]

TECHNOLOGY

Geology

Zirconium and hafnium are always found together in minerals. The earth's crust has been estimated to contain 220 parts per million of zirconium, compared with 4.5 parts per million of hafnium.

Zirconium is a fundamental constituent of a number of minerals and an occasional constituent of others. The well known zirconium minerals are zircon ($ZrSiO_4$) and baddeleyite (ZrO_2). Zircon and baddeleyite are marketed commercially, but zircon is practically the lone zirconium mineral in use.

Zircon is often a minor constituent of granites, pegmatites, and granodiorites, and sometimes a minor constitutent in diabase, basalt, limestone, sandstone, conglomerate, slate, schist and gneiss. Zircon is rarely found in rock in economically minable concentrations. However, weathering and erosion, particularly of granitic rocks, have led to deposition in minable concentrations of heavy-mineral sand along rivers and ocean beaches and in dunes. Heavy-mineral

[2] Italicized numbers in parentheses refer to items in the list of references at the end of this chapter.

sands are found in many parts of the world. Australia is a large supplier of zircon.

Mining and Concentration

Zircon and minor quantities of baddeleyite are recovered commerically from heavy-mineral beach sands or river gravels as coproducts and byproducts of ilmenite and rutile, and occasionally gold, cassiterite, and monazite.

Heavy-mineral sands are usually mined by conventional dredging methods using bucketline, suction, or dragline dredges. The heavy-mineral rougher concentrator may be on the dredge, on one or more barges attached to the dredge or on land. The mineral constituents are usually separated from the rougher heavy-mineral concentrate in a mill on land. Spiral concentrators and electrostatic and magnetic separators are extensively employed in the recovery and separation of zircon.

Numerous flowsheets are in use for separating zircon and other valuable minerals from heavy-mineral sands. Procedures used by the Trail Ridge, Fla., plant of Du Pont to separate zircon from sand containing zircon, ilmenite, rutile, leucoxene, staurolite, sillimanite, kyanite, and other minerals are described briefly as follows (*3*):

Feed from the dredge is pumped to 704 rougher spirals which produce a concentrate for further treatment, middlings for recirculation and retreatment, and tailing reject. The concentrate continues on to 264 cleaner spirals which produce a concentrate for further treatment and middling and tailing for recirculation and retreatment. The concentrate continues to 132 recleaner spirals which produce a concentrate for further treatment and tailing for recirculation and retreatment. The concentrate is scrubbed, dried, and passed through rougher electrostatic separators which produce a concentrate, middling, and tailing. The concentrate is redirected for recovery of titanium minerals, the middling is recirculated for retreatment, and the tailing goes to scavenger electrostatic separators which produce concentrate, middling, and tailing, the latter two being recirculated for retreatment. The concentrate goes to a magnetic separator to remove staurolite and then to spirals to remove sillimanite and kyanite and to produce a zircon concentrate which undergoes electrostatic and magnetic separation, the products of which are titanium-rich reject and zircon.

Metal Production

The deBoer-van Arkel process, first described in 1925, is essentially a refining process, and was adopted by the Foote Mineral Co. in 1945. Using impure zirconium as a raw material, zirconium tetraiodide is formed by reaction with iodine vapor at 200° C. This halide, which is gaseous at this temperature, is transferred to a connecting vessel, leaving behind most impurities in a solid state. At 1,300° C the reaction is reversed, depositing elemental zirconium on a heated filament and regenerating iodine vapor to return to the head of the process (*5*).

A procedure to produce commercial-grade zirconium containing about 2 percent hafnium and nuclear-grade low-hafnium zirconium is described briefly as follows (*2*):

Zircon sand and coke, blended together, are melted in an electric-arc furnace to produce zirconium carbonitride containing about 85 percent zirconium. The carbonitride is chlorinated to crude zirconium tetrachloride for Kroll process reduction to commercial zirconium which contains about 2 percent hafnium, or to nuclear-grade low-hafnium zirconium.

For nuclear-grade zirconium, the crude zirconium tetrachloride is dissolved with a complexing agent and put through solvent extraction, which strips hafnium from the solution. The zirconium component is precipitated and calcined to oxide which is rechlorinated to high-purity zirconium tetrachloride. The zirconium tetrachloride is reduced with magnesium in an inert atmosphere in a Kroll furnace, forming a mixture of zirconium and magnesium chloride for distillation. Magnesium chloride is distilled off while zirconium sponge remains behind. The zirconium sponge is crushed, compacted into consumable electrodes, and vacuum melted in an inert atmosphere into ingot. The ingot is used as consumable electrode to produce second-melt ingot, which is machined and readied for fabrication.

Metal Fabrication

A zirconium ingot weighing 1,000 to 2,500 pounds is forged or cogged at approximately 790° to 970° C on standard equipment into a billet. The billet is conditioned by grinding or by grit blasting and is then hot- or cold-rolled to zirconium plate, sheet, or bars. Hot-rolled products are annealed in a neutral or slightly oxidizing atmosphere at about 790° C for 20 minutes. The hot-rolled products are grit-blasted to remove oxide and acid-pickled to brighten surfaces. The cold-rolled product is vacuum-annealed to regain ductility without oxidizing the surface of the metal.

Zirconium Hydride Production

Zirconium hydride is prepared by exposing zirconium sponge in the ½- to 2-inch size range

to hydrogen at 800° C. Commercial hydrogen is used but must be carefully purified. The product is brittle and is ground dry in an inert atmosphere to the desired particle size.

Processing of Zircon as an Industrial Mineral

Zircon intended for use as foundry facings or refractories is graded and sized, and in many cases wet- or dry-ground; it is then marketed as technical, ceramic, or electrical zircon.

Zirconium oxide is prepared by pelletizing zircon with dolomite and reacting it in a rotary kiln at 1,427° C. The kiln product is a mixture of zirconia and artificial monticellite ($CaMgSiO_4$). The latter is leached with acid to leave a final zirconia product. This product may be stabilized with alkaline-earth oxides, or may be unstabilized (monoclinic) zirconia of high purity; either can be made by using suitable charge proportions.

Other zirconium chemicals—the hydrous or carbonated oxide, the acetate, sulfate, fluorides, zirconyl chloride, organic zirconium complexes, and various zirconates—are usually prepared from the unstabilized oxide.

USES

More than half of the zircon is utilized in its mineral form; the remainder is used to produce zirconium metal, alloys, and compounds.

Zircon has extensive use as refractories, particularly as foundry molds and cores. Other applications are in chemically resistant ware, enamels, electrical insulators and resistors, glazes, glass polish, pigments, heat transfer pebbles, porcelains (*1*), and abrasives.

Zirconium's very low absorption cross section, excellent corrosion resistance at moderately elevated temperatures, good strength, good ductility, ease of fabrication, low radioactivity after reactor exposure (*5*), and very large mineral-resource supply have led to extensive use in nuclear reactors. Powerplants of the first atomic-powered submarine, *Nautilus*, and a number of other naval vessels contain zirconium.

Zirconium's corrosive resistance has led to the development of many applications, particularly in the chemical industry, such as components of heat exchangers and acid concentrators, tanks, shafts, valves, pump housings, fanwheels, high-speed agitators, electrode assemblies, steam-jet exhausters, tubing, pipe and pipe fittings (*6*), spinnerettes used in the textile industry (*5*), and crucibles. Zirconium foil is used in photo flashbulbs.

Numerous zirconium alloy systems have been developed; those commonly known in industry are Zircaloys and ferroalloys. Zircaloys also are used in nuclear reactors. Columbium-zirconium alloy magnets have use in scientific instruments.

Numerous uses have been developed for zirconium compounds (*1*). Besides being used in the production of zirconium metal and alloys, zirconium oxide is used in refractories and abrasives. Other uses developed for zirconia include such applications as hardener for metals; opacifier for glazes, enamels, and X-ray photography; phosphor activation; prolonging life of cathodes of fluorescent lamps; retarding recrystallization of electric-lamp filaments; decreasing the coefficient of thermal expansion, increasing chemical resistance, and absorbing infrared and ultraviolet radiation in certain glasses; electrical insulators and wire-insulating compositions; and removing tellurium and mercury from crude selenium.

Zirconium alkoxides are added to paint to inhibit rust, used as catalysts, as a flexible film coating on stainless steel, as ink stabilizer to promote drying and prevent smearing, and as water repellent for leather and textiles.

In addition to its use in producing zirconium metal, zirconium tetrachloride has applications in catalysis, but most of these uses are trade secrets. Sulfatozirconate is used as a tanning agent to produce high-quality "plump" leather.

Some floor waxes contain zirconium.

BYPRODUCTS AND COPRODUCT RELATIONSHIPS

Zircon is recovered commercially while dredging heavy-mineral sands primarily for ilmenite and rutile; it usually is a coproduct but sometimes is a byproduct. Other merchantable products of these sands include monazite, kyanite, staurolite, and garnet. Placer deposits rarely are worked for zircon alone; each product bears a share of the operating cost.

In the production of reactor-grade zirconium, hafnium is removed as a valuable impurity. High-hafnium zircon such as that from Nigeria increases the yield of hafnium.

ALTERNATE MATERIALS

Stainless steel is an alternate material for nuclear structural applications, whereas aluminum, columbium, and vanadium may be used in place of zirconium for fuel containers. Stainless steel and titanium are substituted for zirconium in many corrosion-resistant industrial applications.

In ferrous metal applications, manganese, vanadium, and several other elements may be

substituted as deoxidants; titanium is a slightly better denitrifier; aluminum and titanium inhibit grain growth as well as zirconium; vanadium and chromium may be substituted to improve low-temperature impact strength (*4*).

Alumina holds promise as a mold aggregate, but is more expensive than zircon. Zircon is an acid refractory. In some instances it can be replaced by silica and olivine.

Titanium oxide and tin oxide may be substituted as opacifiers in ceramic glazes and enamels.

SECONDARY SOURCES AND RECOVERY

Scrap developed from fabricating zirconium is usually remelted into ingot. Very little zirconium and Zircaloy scrap is obtained through scrap dealers for remelting.

RESERVES

The U.S. resource of zircon concentrate containing approximately 66 percent ZrO_2 was estimated in 1961 at 12.6 million tons. The free world resource of zirconium minerals has been estimated at 23 million tons.

The U.S. resource of zircon is in sand deposits associated with titanium minerals except that of New Mexico, Utah, and Wyoming which is in zirconiferous sandstone.

The distribution of the U.S. zircon resource is shown in table 1.

TABLE 1.—*Resource of zircon in the United States, by States*

State	Thousand tons
California	1,500
Florida	7,155
Georgia	345
Idaho	82
Maryland	162
New Jersey	1,520
New Mexico, Utah, Wyoming	290
Oregon	90
South Carolina	1,350
Other States	87
Total	12,581

The free world resource of zirconium minerals is shown in table 2. In addition, there are important deposits in Egypt, the Republic of Senegal, Western Australia, and the Bihar and Orissa provinces of India, but quantitative data are lacking.

TABLE 2.—*Free world resource of zirconium minerals, by countries*

Country	Thousand tons
Australia	2,882
Brazil	2,552
Ceylon	1,000
India	3,360
South Africa, Republic of	564
United States	12,581
Other countries [1]	404
Total	23,343

[1] Includes Republic of Ivory Coast, Republic of Korea, Malagasy Republic, Nigeria, and Uruguay.

SOURCES OF STATISTICAL INFORMATION

Domestic producers, dealers, and primary consumers of zircon are canvassed annually by the Bureau of Mines. Stocks, receipts, production, shipments, and consumption of zircon and of zirconium metal, alloys, and compounds are reported. Foundries are not canvassed for data on zircon.

PRODUCTION, CONSUMPTION, AND TRADE

Production and consumption data on various zirconium products are shown in table 3.

TABLE 3.—*Production and consumption of various zirconium products in the United States*

[Short tons]

Item	1954–58 average	1959	1960	1961	1962	1963
Production:						
Zircon	35,497	(1)	(1)	(1)	(1)	(1)
Zirconium sponge	(2)	1,404	1,423	1,697	1,272	1,022
Zirconium oxide [3]	(2)	(2)	6,907	5,732	4,495	5,283
Zircon and zirconia refractories	(2)	16,500	24,862	20,737	37,100	21,000
Consumption:						
Apparent, zircon	(2)	81,500	89,000	92,100	89,000	[4] 37,500

[1] Figure withheld to avoid disclosing individual company confidential data.
[2] Data not available.
[3] Excluding zirconia used for metal production.
[4] Excludes foundries.

Imports and exports of various zirconium products are shown in table 5. Zirconium ore and concentrate are imported duty free. Unwrought zirconium is dutiable at 12.5 percent, ad valorem.

Imports of zircon are shown in table 4.

TABLE 4.—*U.S. imports for consumption of zircon, by countries*

[Short tons]

Country	1954–58 (average)	1959	1960	1961	1962	1963
Australia [1]	27,195	53,650	29,183	31,225	27,001	50,004
Austria						11
Brazil [2]	658			4		
Canada [3]	63	24	2		1	24
Nigeria	10	868	1,850		544	981
South Africa, Republic of		280	3,133	2,576	3,326	1,523
United Kingdom [3]	35	56	112			
Total: Quantity	27,961	54,878	34,280	33,805	30,872	52,543
Value	[4] $740,296	$1,517,485	$1,233,815	$873,376	$844,939	$1,715,878

[1] Imports from Australia through 1954 were partly in the form of mixed concentrate containing small quantities of rutile and ilmenite.
[2] Concentrate from Brazil includes some baddeleyite.
[3] Believed to be country of shipment rather than country of origin.
[4] 1954 data known to be not comparable with other years.

TABLE 5.—*Imports and exports of zirconium products*

[Short tons]

Item	1954–58 average	1959	1960	1961	1962	1963
Imports:						
Zircon	27,961	54,878	34,280	33,805	30,872	52,543
Zirconium metal	33			(1)	2	(1)
Exports:						
Zircon	3,082	1,511	1,382	1,277	1,666	1,418
Zirconium metal and alloys, crude and scrap	32	40	498	44	72	108
Zirconium and zirconium alloys, semifabricated	2	5	35	45	37	38

[1] Less than 1 ton.

STRATEGIC CONSIDERATIONS

The United States is self-sufficient in zirconium metal, alloys, and compounds and could be self-sufficient in domestic zircon if required, but at higher prices.

Zircon is recovered commercially in Florida which has more than half of the total U.S. zircon resource.

Zirconium sponge is produced in Oregon, Ohio, West Virginia, and Florida. Zirconium ingot is produced in Oregon, Ohio, West Virginia, and California. Most of the zirconium alloy production is in New York, West Virginia, and Ohio.

Zirconia output, excluding that produced for zirconium metal production, is mostly in New York, Alabama, and Ohio.

Large quantities of zircon are imported for commercial use, particularly from Australia, but zircon output in Florida could probably be increased substantially if needed.

GOVERNMENT PROGRAMS

Zirconium mineral concentrate is not being bought by the Government for the national strategic and supplemental stockpiles. Stocks, on December 31, 1964 totaled 1,920 tons of zircon and 16,533 tons of baddeleyite, both destined for disposal.

Zirconium is not acquired for the national strategic stockpile.

PRICES

Quoted prices for zircon concentrate and zirconium in December 1964 follows:

	Price
Zircon:	
Domestic, containing 66 percent zirconia, f.o.b. Starke, Fla., per short ton	$47.25
Imported, containing 65 percent zirconia, c.i.f. Atlantic ports, per long ton	61.00
Zirconium:	
Flash-grade powder, per pound	10.00
Sponge, per pound	4.25–5.00
Sheets, strip, and bars, per pound	10.00–14.00

TAXES

The domestic depletion allowance is 23 percent, whereas the foreign depletion allowance is 15 percent.

TRANSPORTATION

Domestic zircon is shipped in bags or in covered hopper cars; imported material comes in 112-pound bags or bulk.

Zirconium combines readily with oxygen and nitrogen and is quite combustible; in its finely divided state it is even explosive. Burning zirconium is not extinguished by water, carbon tetrachloride, or carbon dioxide; dry chemicals are used to cover and isolate the burning material. Interstate Commerce Commission regulations exist for shipping some forms of zirconium.

RESEARCH

Zirconium has undergone extensive research and development since its emergence as a very desirable metal for nuclear reactor applications.

Much of the work on zirconium has been published by the Government, industry, and various organizations.

Principal features of the Bureau of Mines program on zirconium and hafnium in 1963 were research on extraction, separation, and purification of zirconium and hafnium, and studies on alloys and refractory compounds.

OUTLOOK

The demand for zirconium in nuclear reactors will depend on the future demand for new reactors and how well zirconium outperforms its competitors such as stainless steel and aluminum. Moderate use of zirconium in reactors is predicted, but this market will be relatively small compared with outputs during the early 1960's when, in addition to normal usage, AEC-acquired large quantities of zirconium for testing and stocking.

Modest increases in the demand for zirconium alloys and chemicals are predicted.

Market expansion, especially for zirconium metal, will be stressed. New uses and larger markets in established uses will be sought.

Research will continue on zirconium's basic properties, improvements in processing technology, development of new uses, and testing the metal under duress.

Competition among zirconium producers will be keen, and occasional price reductions of zirconium may result.

There may be greater international competition for zirconium products as industries in other countries continue to develop.

Zircon mining, both domestic and foreign, will continue to expand and modernize to compete for increasing markets, particularly in foundry and refractory applications. No large decrease in the price of zircon is anticipated.

PROBLEMS

Zircon output is not always controllable because zircon is recovered as a byproduct in mining and milling for titanium minerals. Mining and beneficiation problems include sampling procedure, special concentrating methods, tailing disposal, land reclamation, and water pollution control.

Ductile zirconium has only been available for slightly more than a decade. The most pressing problem for zirconium is: How can large markets be developed for the metal? Zirconium metal output has largely been purchased by AEC for limited nuclear-energy applications. This market is in the development stage; consequently some zirconium producers curtail or suspend operations from time to time.

The problem of increasing the demand for zirconium may require solutions to numerous individual problems such as price reductions, lowering high costs of extraction and fabrication, expanding the technology, and testing the performance of zirconium in many diversified applications in industry.

Additional information is needed on the properties of zirconium compounds and production of these materials.

More than half of the zircon consumed in the United States is used in foundries for molding. The zirconium goes to waste since no attempt is made to recover it. Conservation of the zirconium is therefore a problem.

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INDEX AND INFORMATION FINDING GUIDE

The 89 commodity chapters in Bulletin 630 are arranged alphabetically by commodity and conform to a standard outline, but with some deviations and omissions as required for particular commodities. The generalized outline is as follows:

Summary
Background
- Size and organization of the industry
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- Definition of terms, grades, and specifications
- Technology—geology, mining, processing
- Uses
- Byproducts and coproduct relationships
- Alternate materials
- Secondary sources and recovery
- Reserves (domestic and foreign)
- Conservation
- Sources of statistical information
- Production, consumption, and trade
- Strategic considerations
- Government programs
- Prices and costs
- Taxes
- Employment and productivity
- Transportation
- Research

Outlook
Problems
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The commodity index has two main purposes. First it is a guide to the title of the main chapter in which a particular mineral or mineral commodity is reviewed. For example a glance at the commodity index will show that amosite is reviewed in the Asbestos chapter and rutile is reported in the Titanium chapter. As a second purpose the commodity index serves as a guide to any substantial reference to a mineral commodity in a chapter dealing principally with some other commodity. As an example, while most information on copper is in the Copper chapter, the index lists several substantial references to copper in other chapters.

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